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An Investigation of Techniques for Removal of Cyanide from Electroplating Wastes

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16. Abstract: Increasingly stringent stream discharge regulations have prompted an assessment of the current technology available for application to the metal finishing waste treatment problem, specifically in regard to smaller operations. 655 questionnaires were sent to various metal finishing plants, and 50 firms were requested to send samples of the various effluents for analysis. Experimental laboratory and bench scale studies were then conducted on several unconventional wastewater treatment methods, including ion flotation, activated carbon adsorption, acidification volatilization, and solvent extraction. A demonstration pilot plant study was also conducted on the activated carbon process employing actual rinse waters from a zinc cyanide plating operation. The pilot scale activated carbon system was operated at 99% efficiency of cyanide removal, while providing for the complete recovery and regeneration of copper. Cost estimates for both a manual and a semi-continuous carbon sorption process for removing cyanides from cadmium and copper as well as zinc plating rinse waters were formulated for capital, chemical, and net operating costs for a plant treating 10 gpm of wastewater containing 30 ppm of cyanide. (Lowry-Texas)

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Sponsored by

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ENVIRONMENTAL PROTECTION AGENCY

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Prepared by

BATTELLE

Columbus Laboratories

Columbus, Ohio 43201

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ABSTRACT

This report describes work which was conducted on the removal of cyanide from plating rinse waters employing various treatment processes. The study consisted of an initial phase in which information was sought by questionnaire and by wastewater analyses on the type of waste produced by smaller electroplating plants. Laboratory studies were conducted on several nonconventional methods for treatment of these wastewaters, including ion flotation, adsorption on activated carbon, acidification volatilization, and solvent extraction. A demonstration pilot-plant study also was conducted on the activated carbon process employing actual rinse waters from a zinc cyanide plating operation.

The results of the various phases of the study indicated that activated carbon adsorption for cyanide removal may have practical application in many small plating plants. When combined with pretreatment stages for solids removal, effective elimination of heavy metals also can be expected. Further development of the process was recommended in actual plating plant installations.

This report was submitted by Battelle's Columbus Laboratories in partial fulfillment of Grant Project No. 12010 EIE by the Industrial Pollution Control Section, OR&M of the Environmental Protection Agency to the Metal Finishers' Foundation.

Key Words:

Electroplating wastes
Cyanide
Waste treatment
Activated carbon.

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SECTION I

CONCLUSIONS

(1) Although the use of waste treatment systems by small electroplating plants is not yet required in many locations, there is little doubt that more and more stringent treatment of discharges to streams and sewers will be required in the near future. Adequate technology is available for treating these wastes to any required degree of detoxification using conventional processes.

(2) On the basis of the results of this study, several nonconventional processes are technically feasible for the treatment of cyanide wastewaters, including activated carbon adsorption, acidification and volatilization of hydrogen cyanide, and ion flotation. Several other recently developed processes, such as electrolytic oxidation of cyanide and chemical oxidation using peroxides, also appear to be practical for use by the small plater.

(3) The carbon process developed in this study through laboratory and pilot-plant operations utilized actual zinc cyanide plating rinse waters obtained from a small plating company. The systems were operated with removal efficiencies greater than 99 percent for total cyanide. Removal of copper which was added to the rinse water to effect adsorption also was complete. These removal efficiencies compare favorably with other known methods for treating cyanide wastewaters. The system provided for the complete regeneration and recovery of copper and the elimination of cyanide from the wastewater. The cost of chemicals--a major index of process operating costs--was estimated from the early laboratory and pilot-scale work to be in the range of $0.20-0.40 per pound of cyanide treated. With further development, it is considered likely that the cost of chemicals can be reduced to or below $0.30 per pound of cyanide, especially if the process is applied to cyanide waste solutions which contain copper.

(4) Estimation of capital requirements and net operating costs were prepared for both a manually controlled and for a semicontinuous carbon sorption process for removing cyanides from cadmium and copper as well as zinc plating rinse waters. These estimates were based on a wastewater flow of 10 gallons per minute containing 300 ppm of cyanide:

	Manually Operated System	Semicontinuous System
Estimated Capital Required, $	12,000	16,000
Estimated Cost of Chemicals, $/lb CN	0.30	0.30
Estimated Net Operating Costs, $/lb CN	0.21-0.87	0-0.82

The range in net operating costs depends upon the amount of the credit that can be taken for recovery of copper as copper sulfate. The lower estimate of net operating cost accounts for the recovery of copper from the treatment of copper plating rinse waters.

(5) From a practical and economic standpoint, an extension of the present treatment of zinc cyanide wastes using the activated carbon adsorption process has promise of excelling the conventional methods, when applied to the treatment of copper cyanide plating rinse waters and copper cyanide strip solutions, in which case the process might be used for copper recovery as well as cyanide treatment.

SECTION II

RECOMMENDATIONS

This program has involved an evaluation of both conventional and non-conventional processes for the treatment of cyanide rinse waters produced in small electroplating plants. The study has demonstrated that several new approaches for treating cyanide wastewaters show promise as simple and economic processes, especially for use by the small plater. However, it was not within the scope of the program to develop these processes to commercial utilization.

For accurate definition of the full potential of this study in the cyanide waste treatment field, the work of this study should be extended to a demonstration scale. The pilot-scale investigation has in fact demonstrated the feasibility of an activated carbon process for treatment of zinc cyanide rinse waters; several important questions need to be answered:

(1) To what extent will the feasibility of the process be effected for operation with other cyanide wastewaters peculiar to the plating industry? Indications are that the process may be simplified and have greater economic merit if applied to copper plating, brass plating, or copper cyanide stripping waste solutions. The method in its present development has been demonstrated only for zinc cyanide wastewaters.

(2) How can regeneration of the carbon after adsorption of copper cyanides be made more effective and less time consuming? The present method obviously must be improved to fit into a practical plant operating schedule. Moreover, to what extent will improved regeneration or alternative procedures enhance the practical and economic feasibility of the process. Battelle has proposed to Metal Finishers' Foundation a program to investigate other means of regenerating the carbon, including electrolytic methods.

(3) What are the precise economic criteria such as labor, instrumentation, and analysis governing the economic evaluation of this process, and how will it compare to conventional treatment after the required further development?

It is recommended that these factors be established firmly by extending the studies of the carbon adsorption process in full-scale demonstration equipment. It also is recommended that a logical next step be an extension of the method to treatment of copper plating rinse waters. This application appears to be feasible and one which may result in simplified procedures and improved economics. Very probably the development would involve some minimum of additional laboratory study in conjunction with the operation of the demonstration plant.

SECTION III

INTRODUCTION

Many industries in the heavily industrialized areas of the United States contribute substantially to the growing problem of water pollution. In many cases the wastes generated by industrial sources are carbonaceous and can be treated by biological methods or by incineration techniques. In other cases, the wastes are largely inorganic materials which are difficult to dispose of by these techniques. Some of the most troublesome wastes are those generated in the production of inorganic chemicals and in other metallurgical operations. In the latter category, considerable attention has been directed toward abatement of pollution from waste pickle liquor from the steel industry, and from metal-finishing wastes.

Electroplating and metal-finishing waste streams can contribute directly to stream pollution resulting from the content of toxic and corrosive materials such as cyanide, acids, and metals. Indirect effects also have been noted in the deleterious effect these components exert on biological sewage treatment systems. Federal, state, and municipal regulations fixing the allowable concentrations of the waste components to these discharges already have been established. The restrictions are fairly rigorous at present. There is indication that they will, in many places, be made more rigorous in the future. Enforcement of regulations may be expected to become increasingly strict.

There is ample technology available for treating cyanide wastewaters to any required degree of detoxification. The conventional treatment methods have been developed primarily for large electroplating plants where the relatively high cost of treatment can be absorbed more readily. Economical methods have not been developed for the treatment of wastes from the relatively small electroplating shops. Currently many of these plants discharge their wastes into the city sewers, and so depend upon the municipal sewage plant for the removal of toxic materials.

More restrictive sewer ordinance and receiving water standards are major factors that make development of economical techniques for treating the effluents from small electroplating facilities highly desirable. Another factor is the potential recovery of valuable metals from these waste streams.

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The Pollution Abatement Committee of the Metal Finishers' Foundation being acutely aware of this problem, authorized Battelle to undertake a study of existing hydrometallurgical techniques to determine their applicability to the treatment of wastes from the smaller electroplating plants. This study, as proposed to the Metal Finishers' Foundation, was comprised of two phases:

Phase 1. Preliminary Experimental Study
Phase 2. Demonstration Plant Study.

In each of these phases, chromium wastes and cyanide wastes were given separate study. This report presents the results, conclusions, and recommendations of the study on cyanide wastes. A similar report dated July 31, 1970, was submitted on chromium wastes.

The first phase of this work on cyanide containing wastes was, in effect, a screening study, the overall objective of which was to pinpoint the processes best adapted technically and economically to the treatment of cyanide wastes typical of those generated by the smaller plater. In this phase of the study, a thorough review of the present state of the art in the treatment of cyanide waste was conducted; wastes from a selected sample of smaller plating establishments were characterized for volume and composition; and several nonconventional approaches available to the smaller plater for treating his wastes were evaluated experimentally As a result of this preliminary phase study, it was concluded that a novel technique--activated carbon adsorption--showed promise of excelling the conventional process as a practical and economic method for treating cyanide wastes from the typical smaller shop.

In the second phase of the study, this carbon adsorption process was investigated on the pilot-plant scale. The pilot plant was set up in an actual plating plant (a member of the National Association of Metal Finishers) and operated on this plant's normal zinc-cyanide rinse waters.

This overall study on chromium and cyanide emphasized only these two contaminants in the evaluation of experimental processes. This, of course, overlooks other important contaminants, particularly heavy metals, which would be carried over in the combined wastewater stream. Although techniques were developed which might also provide effective removal of heavy metals in addition to chromium and cyanide, the experimental development of the techniques as an overall waste treatment approach was beyond the scope of the current program.

SECTION IV

BACKGROUND INFORMATION

State of the Art of Metal-Finishing Waste Treatment

One of the initial efforts in this program was devoted to a survey of the open literature pertaining to waste treatment in the metal-finishing industry. This state-of-the-art survey emphasized such aspects as the nature of electroplating and metal-finishing wastes, current restrictions on their disposal, and conventional methods available for treatment of these wastes. The survey is presented in detail as a separate progress report on this program, designated 12010 EIE, dated November 15, 1968. It is not included within this report. However, for the purpose of comparing waste-treatment processes, a description of the conventional methods determined by this survey is included in the appendix. The review of these methods is intended to provide facts for the guidance of the smaller plater in the selection of a waste treatment process. It should be pointed out, however, that these methods were developed for use in electroplating plants having large volumes of wastewater. The use of these methods for treating low volumes of wastewater would certainly be feasible technically, but could be impractical or uneconomical for the smaller plater.

Current Practices in Small Electroplating Plants

Production Characteristics

One of the major efforts during the initial phase of the program was the accumulation of considerable data on the operating characteristics of small electroplating plants. These data were obtained by surveying member plants in NAMF via questionnaires. The survey emphasized primarily the extent of chromium- or cyanide- plating operations and certain aspects of the operations such as rinsing methods, disposal methods, chemical and water usage, etc. Questionnaires were sent to 655 U. S. members (foreign members were not included). In addition, 50 firms were asked to submit samples of combined and segregated rinse waters from their plant. Although only about 200 questionnaires were returned, a large number of firms were not involved in chromium or cyanide plating.

The basic production characteristics of NAMF member plants based on this survey are summarized in Tables 1, 2, and 3. Table 1 shows the number of plants which have chromium and/or cyanide plating operations. These

TABLE 1. SUMMARY OF NAMF MEMBER PLANTS IN WHICH CHROMIUM AND/OR CYANIDES ARE USED

	Number of Plants	Percent of Total
Plants with chromium only	24	13
Plants with cyanide only	11	6
Plants with both chromium and cyanides	151	81
Total	186	100

TABLE 2. SUMMARY OF RINSING PRACTICES IN NAMF MEMBER PLANTS

	Number of Plants	Percent of Total
Separate chromium and cyanide rinse circuits	84	47
Combined chromium and cyanide rinse circuits	94	53
Practical to separate wastes	71	42
Impractical to separate wastes	100	58

TABLE 3. SUMMARY OF DISPOSAL METHODS USED BY NAMF MEMBER PLANTS

	Number of Plants	Percent of Total
Municipal sanitary sewer	143	75
Storm sewer	24	12
Land disposal	5	3
Lagooning	3	2
Natural stream, lake, etc.	10	5
Others	6	3
Total	191	100

data indicate that a large majority of the plants (81 percent) do both chromium and cyanide plating.

Table 2 shows the number of plants which currently have separate or combined rinsing circuits and whether or not it would be practical to separate these wastes. Table 3 indicates the current distribution of plants that employ sanitary sewers, lagoons, natural water bodies, etc., for disposal of wastewaters. These data indicate that most of the plants use sanitary or storm sewers for disposal.

It is reasonable to presume that the response to the questionnaires constitutes a valid sample and that the information obtained is applicable to the association as a whole and possibly to the entire smaller shop plating industry.

Waste Effluent Volumes and Compositions

The level of contaminants in wastewater from electroplating operations and the total volume of these wastes are also important factors in the evaluation of waste-treatment processes for small plating plants. Since this information is almost unavailable in the literature, the waste survey was used to provide data on these factors. NAMF member companies were asked to report their annual consumption of plating chemicals containing chromium and cyanide and the total annual water usage within the plant. For the purpose of estimating the amount of these plating chemicals which eventually appear in the wastewater, a loss factor of 80 percent was selected for both the chromium and cyanides (U. S. Bureau of Mines Information Circular 8058).

Based on this assumption, calculations were made of the total chromium, cyanide, and water discharged by each particular plant. A summarization of these data for all plants surveyed is shown in Figures 1 and 2. These graphs are important in establishing the approximate position of a particular plant within the industry and can be used to provide the following generalizations with regard to waste treatment methods. They are of importance in the assessment of:

(1) The general levels of chromium and cyanides likely to be discharged in the plant's wastewater

(2) The approximate annual cost for destruction of these contaminants within various segments of the industry

(3) Areas where recovery of plating chemicals and water should be considered.

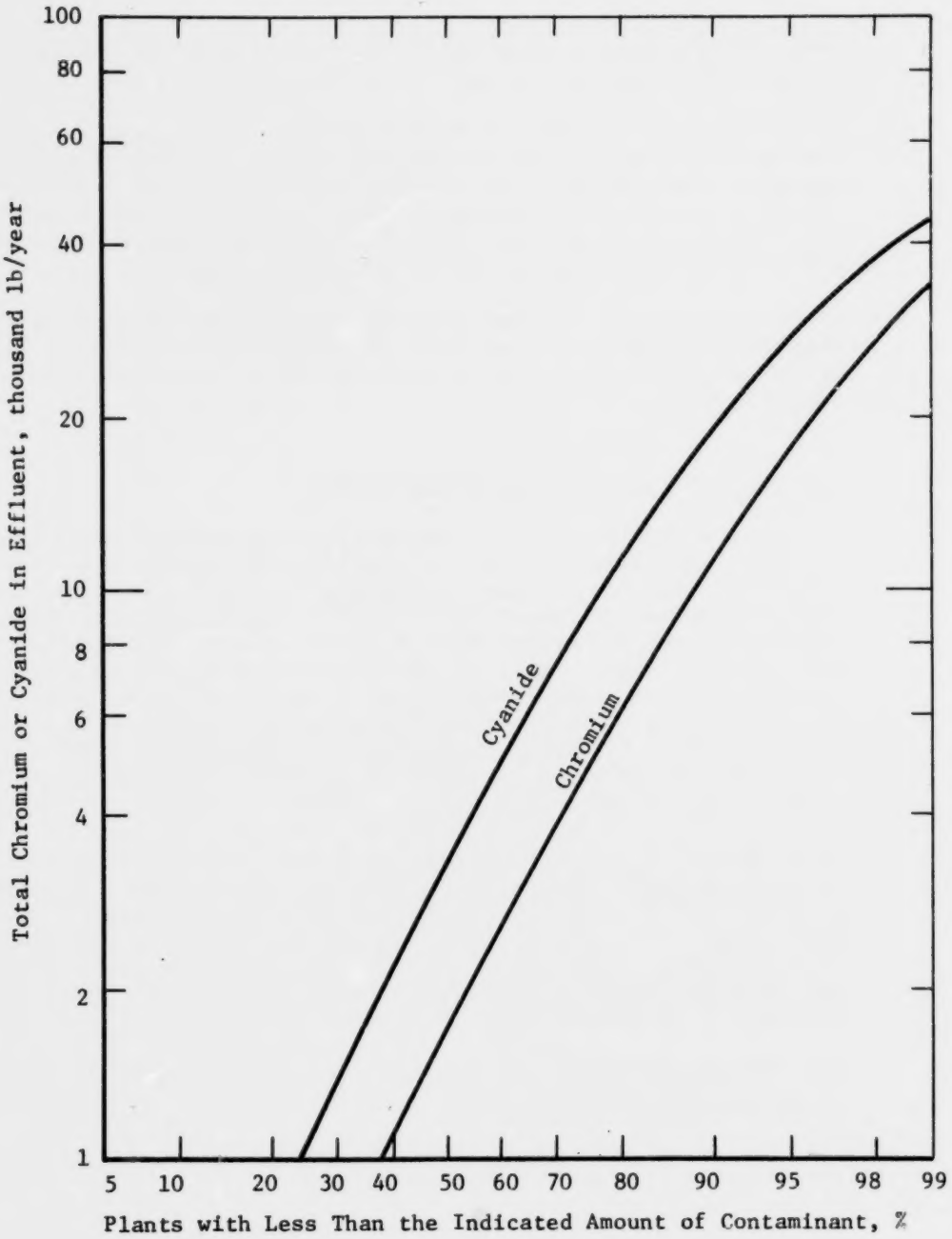

FIGURE 1. CALCULATED LEVELS OF CHROMIUM AND CYANIDE DISCHARGED BY NAMF MEMBER PLANTS

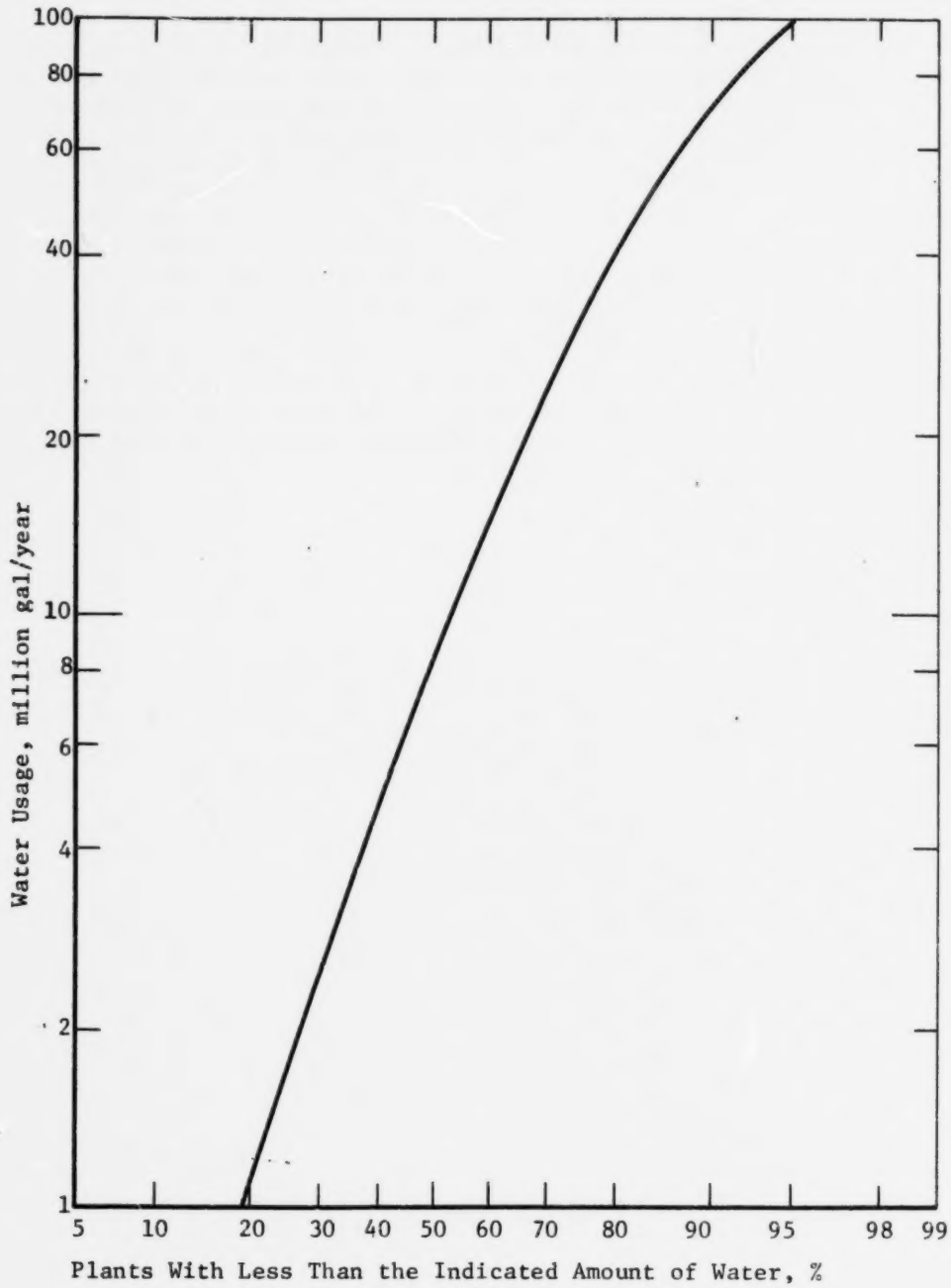

FIGURE 2. WATER USAGE BY NAMF MEMBER PLANTS

In addition to the data shown in Figures 1 and 2, considerable data also were obtained on the actual composition of rinse waters generated by NAMF member plants. Selected plants submitted samples of their waste streams, and these samples were analyzed to determine concentrations of cyanide, chromium, and other metals. Analytical data on chromium and cyanide levels in various waste streams are summarized in Table 4. Typical analyses for heavy metals in effluents from various plants are shown in Table 5. The data on chromium and cyanide indicate that cyanide concentrations are two to three times higher than chromium concentrations for combined effluents, which supports those data shown previously in Figure 1. Generally, it can be stated that concentrations will range from 10 to 100 ppm for either chromium or cyanide. Heavy metal concentrations, by contrast, generally fall below 10 ppm with the possible exceptions of copper and nickel. These elements were the major heavy metals found besides chromium in the particular samples which were analyzed.

TABLE 4. CONCENTRATIONS OF CHROMIUM AND CYANIDE IN VARIOUS WASTE STREAMS FROM NAMF MEMBER PLANTS(a)

Type of Sample	Number of Samples	Total Chromium, ppm(b)		Total Cyanide, ppm(c)	
		Range	Average	Range	Average
Separate chromium stream	9	15-70	41	--	--
Separate cyanide stream	7	--	--	9-115	72
Combined effluent	28	0-49	11	1-103	28

(a) Based on actual analyses by atomic adsorption and standard chemical techniques.

(b) Includes chromium contained in both the liquid and solid fractions of the sample.

(c) Cyanides in the liquid fraction only.

TABLE 5. TYPICAL CONCENTRATION OF HEAVY METALS IN COMBINED EFFLUENTS FROM SEVERAL NAMF MEMBER PLANTS

	Concentration of Indicated Component, ppm(a)				
	Cu	Zn	Cd	Fe	Ni
Plant No. 4	31.0	5.0	<0.5	2.0	9.0
Plant No. 7	2.0	10.0	1.0	2.0	5.0
Plant No. 12	10.0	3.0	4.0	<2.0	58.0
Plant No. 15	36.0	<0.5	1.0	4.0	24.0
Plant No. 21	7.0	0.2	<0.5	2.0	23.0

(a) Based on analyses of samples by atomic adsorption techniques.

SECTION V

EXPERIMENTAL WORK

Phase 1: Preliminary Experimental Laboratory and Bench-Scale Studies

General Scope of Investigation

The initial phase of experimental work was limited to the investigation of nonconventional methods that might be applicable to the treatment of cyanide rinse waters; the conventional methods of treatment having been thoroughly studied by numerous investigators for many years. At the outset of the program, the two most promising of the nonconventional approaches appeared to be:

(1) Ion flotation
(2) Liquid-liquid extraction.

These two approaches and a third--activated carbon adsorption--received major attention in the experimental program. During the course of the study, other nonconventional approaches were suggested and examined briefly. The nonconventional processes tested experimentally during this program are listed in Table 6, and are described in the following sections of the report.

TABLE 6. TECHNIQUES EVALUATED EXPERIMENTALLY

	Free Cyanide	Applicability, complex cyanides				
	Sodium	Zinc	Cadmium	Iron	Nickel	Copper
Ion Flotation	x		x	x	x	
Liquid-Liquid Extraction	x	x	x			
Acidification Volatilization	x	x			x	x
Activated Carbon Adsorption	x	x		x		x

Ion Flotation Studies

General Description of Method. Of the various techniques studied during this program, ion flotation probably is the most recently developed process. The technique of separating ions from aqueous solutions by

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flotation has been recognized only for about 20 years. During this time, however, it has received significant development effort and is now becoming known as one of the basic chemical engineering unit processes.

Ion flotation is basically a combination of conventional mineral flotation and ion-exchange processes. In mineral flotation, for example, finely divided solid particles are separated from a bulk solution by attachment to small air bubbles introduced into the liquid. The bubbles rise to the liquid surface, collapse, and form a froth which contains the solid material in concentrated form. An identical procedure is used in ion flotation to separate and concentrate ions from solution rather than solid particles.

The mechanism of bubble attachment in both flotation techniques is accomplished through the addition of a suitable collector. These collectors usually are some type of organic chemical having surface-active properties and are selective for only certain compounds. In addition to surface activity, the collectors for ion flotation have an inorganic group which ionizes in aqueous solutions and tends to make the collector partially soluble. The exchange of ions between the collector and solution is the basis for separation of certain ions from the solution.

Because ion flotation is especially effective for extremely dilute solutions, it was given initial emphasis during the experimental program. Its simplicity and low equipment costs enhanced its attractiveness for meeting the needs of the smaller plater.

Equipment and Procedure. The experimental apparatus for the study of the ion flotation technique consisted of a specially designed glass flotation cell (see Figure 3).

The glass cell was fabricated from a standard 500-cc graduated cylinder by installing ports for injecting flotation collector solution via a syringe and for withdrawing samples of the bulk solution. The cell contained an air dispersion tube which was made of fritted glass with a porosity of 25 to 50 microns. During flotation, the air was admitted at a constant rate and was measured by a rotameter. The cell also was provided with an overflow tube which could be used to collect any foam produced during an experiment.

Generally, experiments were conducted with a 300-cc volume of solution to be floated. The procedure used in conducting the majority of experiments was as follows:

(1) The cell was filled with 300 cc of the particular solution under study.

(2) The required flow of air was started (in most cases, a rate of 450 cc/minute was used).

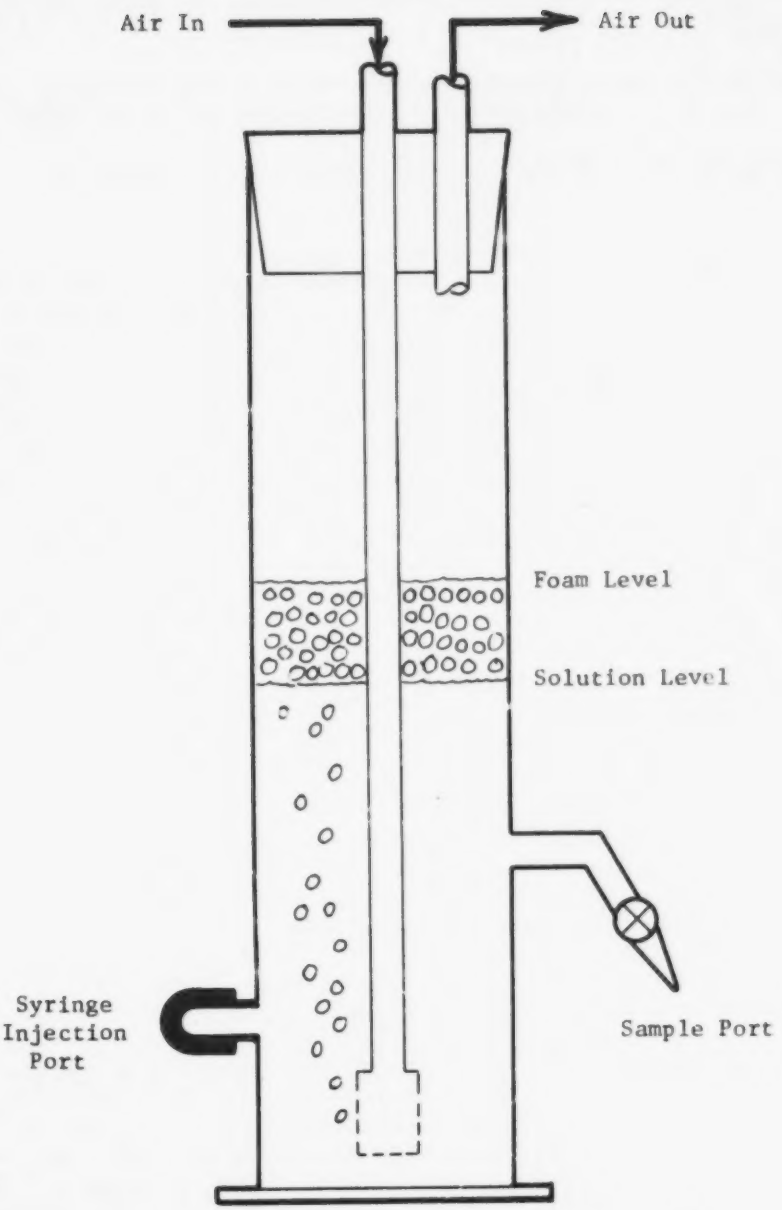

FIGURE 3. SKETCH OF FLOTATION CELL

(3) A preselected volume of collector solution was injected via the syringe port.

(4) After sufficient time had elapsed (generally 10 or 20 minutes), samples of the treated solution were obtained and saved for chemical analyses.

(5) Steps (3) and (4) were repeated until no further change occurred or until a specified total quantity of collector had been added.

(6) Samples were analyzed and the percentage extraction calculated.

Results and Discussion. The initial experiments on ion flotation were conducted with the objective of screening several possible collectors which might be effective for removal of complex metal cyanides. The complex cyanide ion, being negatively charged, required the addition of an anionic collector in order to effect flotation. For the purpose of selecting a suitable collector, a total of seven anionic collectors were evaluated during this preliminary experimentation. The compounds selected for study consisted of primary, tertiary, or quaternary-ammonium compounds containing a long chain organic group of between 10 and 16 carbon atoms.

The preliminary series of experiments was conducted with initial solutions containing 10 ppm cyanide and either 10.8 ppm cadmium or 5.64 ppm nickel as the complexing material. Results are shown in Table 7.

It was found that nickel cyanide complexes could be removed much more effectively than cadmium cyanide complexes. With nickel cyanide solutions, extractions over 90 percent were obtained with several flotation collectors; the best extraction obtained with cadmium cyanide solutions was 57 percent. Although some cyanide was extracted from cadmium cyanide solutions, it was not certain whether this occurred by flotation or because of volatilization of HCN from the solution. Comparative tests (described in a subsequent section of this report) indicated that simple aeration at pH 6 can result in a 50 percent removal of cyanide as HCN in 1 hour from cadmium solutions initially containing 10 to 100 ppm of cyanide; with nickel solutions at comparable concentrations no removal of cyanide as HCN was observed.

Flotation runs also were made on solutions containing iron cyanide complexes formed by the addition of either ferrous or ferric sulfate to a sodium cyanide solution. Typical data for several experiments are shown in Table 8. Note that high extractions were obtained only when the solution was prepared by adding ferrous iron to a basic cyanide solution. In this case the characteristic blue ferrocyanide complex or "Prussian blue" was formed and this material appeared to float easily. In slightly acid solution, the complex between ferrous or ferric iron and cyanide did not form to an appreciable extent and low extractions were obtained.

TABLE 7. EXPERIMENTAL DATA ON VARIOUS COLLECTORS FOR FLOTATION OF CADMIUM CYANIDE AND NICKEL CYANIDE COMPLEXES

Collector Used	Cadmium Cyanide Runs				Nickel Cyanide Runs			
	Amount Used, cc[a]	ppm CN		Indicated Percent Removal	Amount Used, cc[a]	ppm CN		Indicated Percent Removal
		Initial[b]	Final			Initial[c]	Final	
(1) Dodecylamine HCl	4.0	10.0	5.25	47				
(2) Tetradecylamine HCl	2.0	10.0	6.25	37	2.0	10.0	0.75	93
(3) Hexadecylamine HCl	2.0	10.0	7.50	25				
(4) N,N-Dimethyldodecylamine HCl	4.0	10.0	6.75	32	3.0	10.0	0.75	93
(5) Decyltrimethylammonium bromide	4.0	10.0	4.25	57	2.0	10.0	7.50	25
(6) Ethylhexadecyldimethylammonium bromide	0.5	10.0	7.75[d]	22	0.5	10.0	0.50[d]	95
(7) Hexadecylpyridinium chloride	0.5	10.0	7.50[d]	25	1.0	10.0	1.00[d]	90

(a) Solutions were made by dissolving collector in isopropanol and adjusting to 20 gpl. The amine collectors also were neutralized with HCl to a pH of 7.

(b) Initial solutions also contained 10.8 ppm cadmium as cadmium chloride.

(c) Initial solutions also contained 5.64 ppm nickel as nickel sulfate.

(d) Excessive foaming occurred during these runs causing loss of some solution.

TABLE 8. FLOTATION DATA ON IRON CYANIDE SOLUTIONS

Expt. No.	Initial Solution			pH During Flotation(a)	Final Solution Analyses,(b) ppm CN	Apparent Percent Extraction
	ppm CN	ppm Fe	pH(a)			
16A	10.0	3.58 ferrous	Basic	4.0	1.25	87.5
16B	10.0	3.58 ferrous	Acid	4.3	7.75	22.5
16C	10.0	3.58 ferric	Basic	4.0	6.25	37.5
17A	10.0	3.58 ferrous	Basic	8.4	2.35	76.5
17B	10.0	3.58 ferrous	Basic	6.5	1.95	80.5
17C	10.0	3.58 ferrous	Basic	5.1	2.10	79.0
17D	10.0	3.58 ferrous	Basic	4.0	2.65	73.5
18A	10.0	3.58 ferrous	Basic	≈4	2.70	73.0
18B	10.0	5.37 ferrous	Basic	≈4	1.05	89.5
18C	10.0	7.16 ferrous	Basic	≈4	1.25	87.5
18D	10.0	3.58 ferrous 3.58 ferric	Acid	≈4	9.50	5.0

(a) Adjustments of pH were made by adding dilute HCl or NaOH.

(b) Solutions were floated by adding 0.5 cc of tetradecylamine collector and aerating for 10 minutes.

In subsequent experiments, attempts were made to obtain more efficient removal of cyanide from solutions containing either a nickel cyanide complex or an iron cyanide complex. Variations were made in flotation conditions, such as concentration, pH, and type of collector. To expedite the evaluation of these experiments, results were based primarily on visual observation of the extent of removal of the colored cyanide complexes. Selected samples showing high color removal then were analyzed for residual cyanide.

In general, the results of these experiments did not show an increase in the level of cyanide removed over previous experiments. The extent of cyanide removal appeared to be related more to variables affecting formation of the complexes than to variables affecting flotation. The formation of the blue ferrocyanide complex, particularly, was affected by concentration in addition to pH. At concentrations of 100 ppm cyanide, this material tended to flocculate more readily and could not be floated effectively with any collectors. At 10 ppm cyanide, the complex appeared more colloidal and high removals were achieved. Although these studies did not develop an optimum set of conditions for the removal of cyanides, the flotation method showed considerable promise and was considered as an alternative process for further investigation during the remainder of the program.

Liquid-Liquid Extraction Studies

General Description of Method. The liquid-liquid extraction process as it might be applied to metal-finishing wastes is shown in Figure 4. The waste or aqueous phase follows the solid line path through the system into the first-stage mixer (Item 2 in the diagram), then to the first-stage settler (4). Here the phases separate and the aqueous phase now partially depleted of its contaminant passes through the second-stage mixer and settler (5 and 3) where virtually all the remaining contaminant is removed. The organic phase containing the extracting compound passes through the two-stage extraction system countercurrent to the aqueous phase along the path indicated by the dashed lines through the two stages of mixing and settling (5, 3, 2, 4, and 8).

As it issues from the settler (4) it is sent to a regeneration stage (8 and 9) where it is stripped of its load of contaminant and restored to its original composition. The regenerated organic is then recycled back to the extraction stages (6). In the stripping or regeneration section, the stripping agent is constantly recirculated through the mixer-settler (8 and 10). Periodically enough of the stripping solution now loaded with the contaminant is removed from the circuit for subsequent treatment (11).

The process outlined in Figure 4 is merely an example. Numerous variations in flow patterns, number of stages, etc., are possible.

Equipment for liquid-liquid extraction too can be varied. The equipment implied in Figure 4 is the so-called horizontal type, mechanically agitated

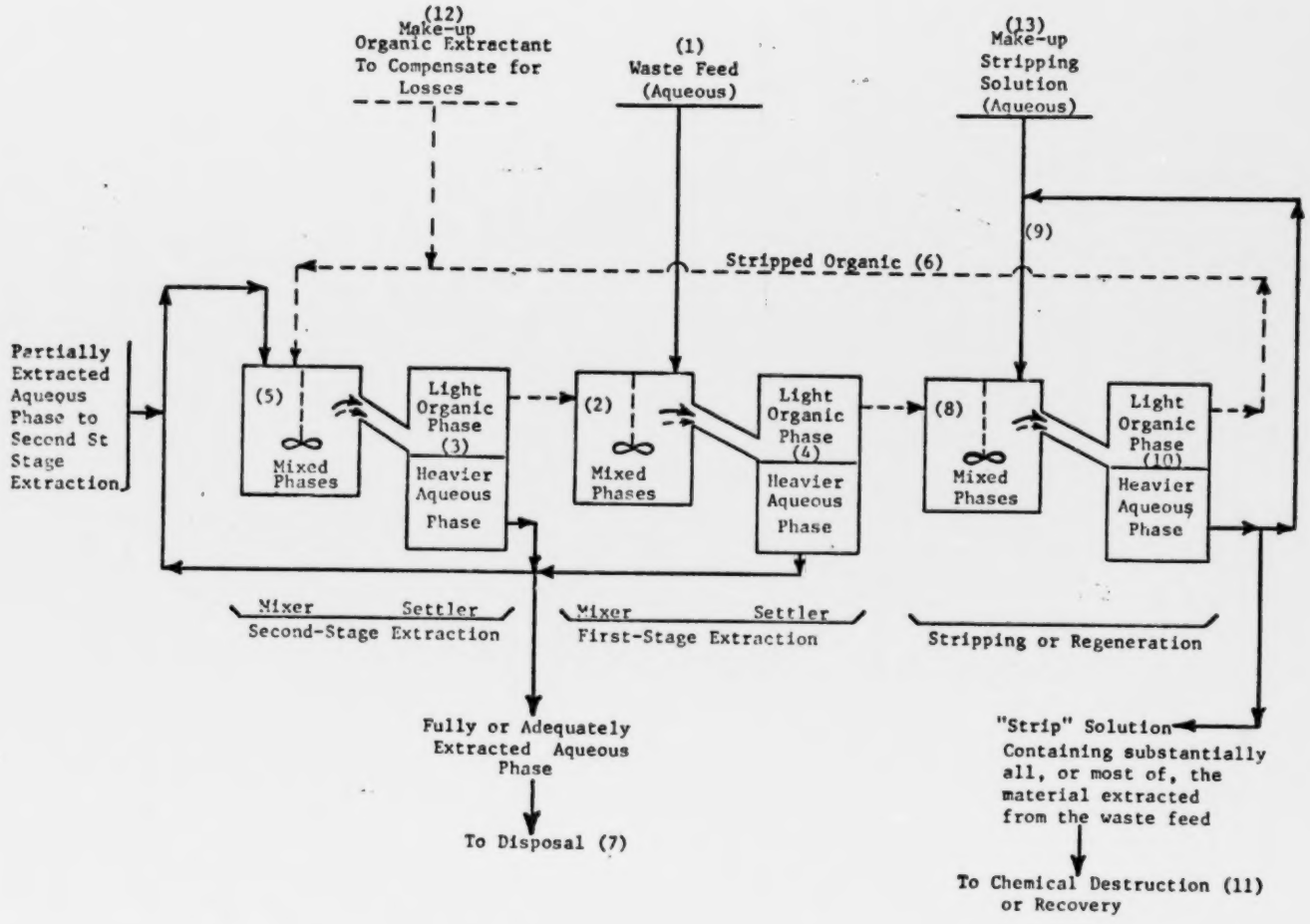

FIGURE 4. EXAMPLE OF TWO-STAGE EXTRACTION, SINGLE-STAGE STRIPPING LIQUID-LIQUID EXTRACTION PROCESS

mixer-settler, in which in each stage the phases are intimately dispersed in one vessel by agitation and then permitted to flow by gravity to another settling vessel for phase separation. Each stage, therefore, requires two separate vessels. Other types of mechanical mixer-settlers may be used. These include the vertical type in which the stages are superimposed in a single vertical shaft with a central axle for driving the agitators in each mixing section and baffled tanks similar in nature to the apparatus used in the laboratory. There are several other types of liquid-liquid extraction equipment which probably also would be applicable to the treatment of metal-finishing waste. These include

(1) Various types of columns in which no agitation is employed, such as perforated plate columns, bubble cap columns, packed columns, and spray columns. This apparatus might possibly be applicable to the treatment of metal-finishing wastes.

(2) Mechanically agitated columns, such as the so-called pulsed column. These would be applicable to the treatment of metal-finishing wastes also, but would be more costly than spray columns.

(3) Centrifuge types in the contacting or mixing. Settling is greatly accelerated making possible high treatment rates and consequently reduced equipment sizes. These types generally are expensive, but require less floor space than the other types.

Chemistry of Liquid-Liquid Extraction. The chemistry involved in liquid-liquid extraction can probably be most clearly explained by an example. For the extraction of cyanide, a number of organic compounds would be satisfactory. The one investigated most thoroughly in the laboratory campaign was the so-called Alamine 336, manufactured by General Mills. Another which was investigated to a lesser extent, but which exhibited as much promise, was Amberlite LA1, manufactured by Rohm and Haas. The former is a tertiary amine, the latter a secondary amine.

The chemistry of cyanide removal by liquid-liquid extraction is not well defined. One reason for this is that the cyanide radical may exist in a number of species in waste solutions, either as free dissolved hydrocyanic acid, as the so-called free cyanide (e.g., sodium cyanide), or as a number of metallic cyanide complexes with such metals as copper, nickel, iron, zinc, and cadmium. Each of these species could be expected to react somewhat differently with the organic extractants and to combine with them in differing proportions.

A brief review of the literature on the chemistry of cyanide adsorption by ion exchange processes, which is analogous to the liquid-liquid extraction process using amines, indicates that the chemistry is not known very precisely. It can be surmised that the reactions which would occur between any of the species in which cyanide would exist in water solutions would react conventionally according to such equations as:

R_4NCl	+	NaCN	→	R_4NCN	+	NaCl
Quaternary amine chloride compound such as Aliquat 336		Free sodium cyanide as in waste liquor		Compound of amine with cyanide		Sodium chloride dissolved in aqueous phase

$4R_4NCl$	+	$Na_4Fe(CN)_6$	→	$(R_4N)_4Fe(CN)_6$	+	$4NaCl$
Quaternary amine chloride		Sodium ferrocyanide as might be intentionally formed in waste		Compound of amine with ferrocyanide ion		Sodium chloride

The extent to which such reactions take place has not been determined. There is evidence in the literature on the ion exchange absorption of cyanide and cyanide complexes that the chemistry involved is not clear cut and probably not precisely understood.

Requirements for Feasibility. For liquid-liquid extraction to be feasible in the treatment of metal-finishing wastes, these conditions would have to be met:

(1) The extraction of cyanide from rinse waters should be virtually complete. Although there may at present be a certain laxity in legislation and enforcement, the day may come when every plater may be required to satisfy limits as low as 1 ppm of cyanide. An acceptable liquid-liquid extraction process would have to be capable of meeting such limits.

(2) Reagent recovery by stripping should be efficient.

(3) The stripping operation should produce a greatly concentrated solution of the contaminant either for recovery or chemical destruction.

(4) The treated effluent solution should be sufficiently free from organic contaminants such as oil to satisfy local restrictions. Present restrictions on oil are variable, ranging from zero to some nonspecific quantity described in such terms as "none making the water unsuitable for the use indicated". It is the very nature of liquid-liquid extraction in which oily substances, such as kerosene, are intimately dispersed in the waste, to introduce some oil into the water phase. The process should operate, therefore, in such a manner that the "oily substance" content of the discharged waste is within permissible limits. The control of the oil content of the treated effluent might be important if the water were reused, even in part, for rinsing, owing to the possible effects on work quality.

(5) The operation should be relatively simple and routine requiring a minimum of time and attention by the plater:

(6) Costs, both capital and operating, should be reasonable.

Equipment and Procedure. Preliminary batch experiments were made in separatory funnels, by the conventional single-stage procedure. In these runs, measured quantities of the aqueous and organic phases adjusted to the desired pH level were mixed. The mixture was permitted to stand for 20 minutes to effect phase separation, and the treated aqueous phase was analyzed to determine its cyanide content.

Subsequent mixer-settler runs were made in the apparatus shown in Figure 5, which provided three stages of extraction, with the aqueous phase being fed into the righthand mixing compartment. Agitation by laboratory stirrers was provided in each stage. The treated aqueous solution was overflowed from the lefthand settling compartment and the "loaded" organic was aspirated by suction from the righthand settling compartment.

The runs were made at various flow rates, volumetric ratios of aqueous to organic, and composition of aqueous and organic solutions.

Results and Discussion. Initially a series of screening experiments to determine suitable reagents was made. These indicated that incomplete extraction of cyanide occurred with primary, secondary, and tertiary amines, as indicated by qualitative testing of treated solutions with silver nitrate. A tertiary amine salt, Aliquat 336, manufactured by Rohm and Haas, however, indicated some promise in these experiments, and was selected for subsequent testing. The results of batch experiments using this on various soulutions are summarized in Table 9. These results indicated that Aliquat 336 has potential as an extractant for cyanide at high pH values. The results also indicated that complexed cyanides were more effectively extracted than the simple cyanide.

To determine the possibility that multiple-stage extraction might produce an effluent below 1 ppm in cyanide, several experiments were made in the mixer-settler. These runs were made on solutions prepared from reagent-grade chemicals to simulate rinse waters that might be obtained from copper and zinc cyanide plating lines. The conditions and results of these mixer-settler experiments are shown in Table 10.

These results indicated that high extractions were possible on both zinc and copper cyanide solutions at elevated pH. However, in neither case was the cyanide consistently reduced to the desired 1 ppm level. In Experiment 75-76 (zinc cyanide solution) which was run for 210 minutes, extremely low cyanide values in the effluent showed as much as 5 ppm of cyanide. A similar situation occurred in Experiment 82 (copper cyanide solution). This erratic behavior indicates that some factor in the laboratory system was not under proper control. While it is believed

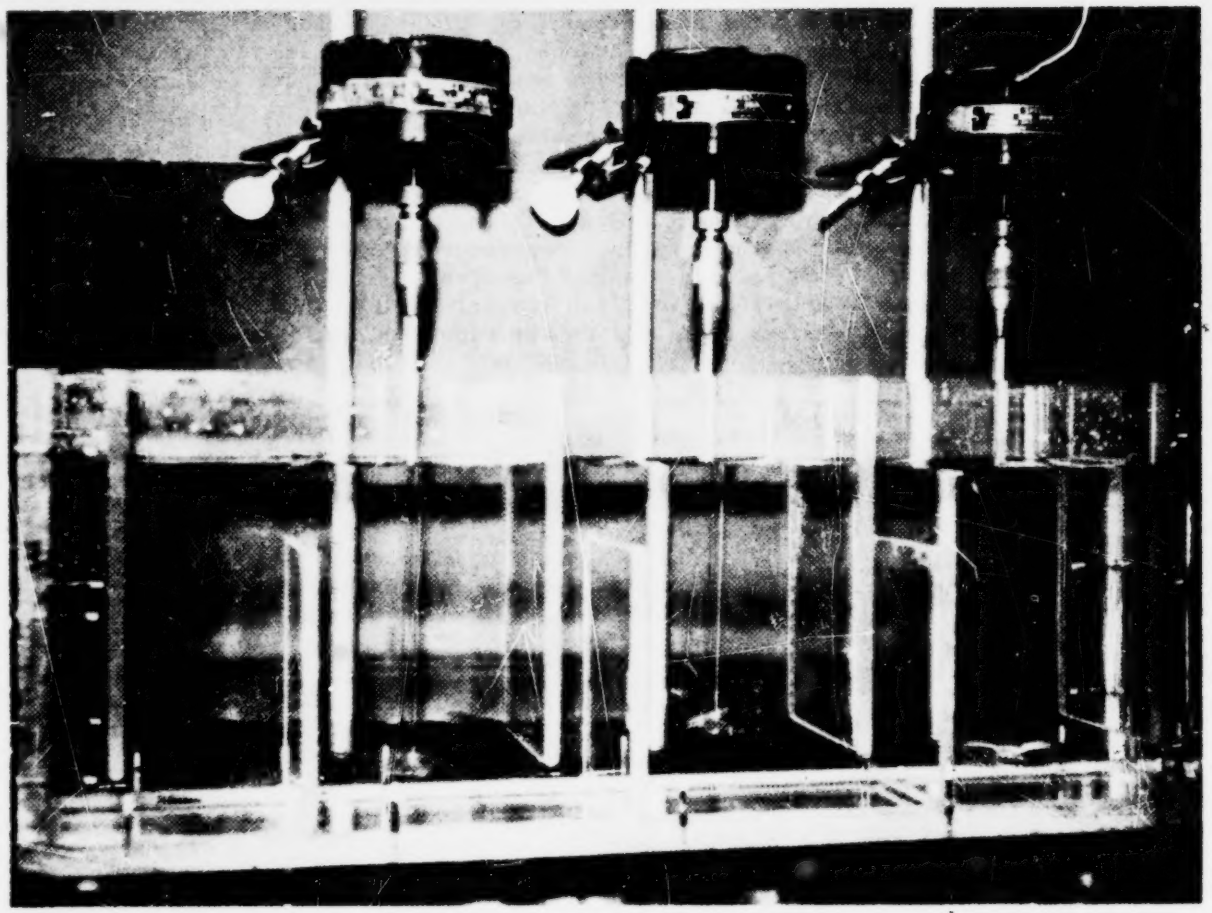

FIGURE 5. BENCH-SCALE MORRIS-TYPE CONTACTOR FOR CONTINUOUS LIQUID-LIQUID EXTRACTION EXPERIMENTS

TABLE 9. SUMMARY OF BATCH EXTRACTION EXPERIMENTS ON CYANIDE SOLUTIONS USING ALIQUAT 336[a]

Expt. No.		Aqueous Phase ppm CN	Aqueous Phase Volume, ml	Aqueous Phase pH	Organic Phase Volume, ml	Organic Phase pH	Organic Phase ppm CN	Cyanide Extraction, percent
48-1	Sodium cyanide	100	100	7.0	55	4.5	38	62
48-2[b]	Sodium cyanide	100	100	8.5	55	5.5	25	75
49-2[c]	Sodium ferrocyanide	100	100	6.8	55	3.3	24	76
43-2[d]	Potassium ferrocyanide	100	100	6.2	55	2.2	2	87
43-3[d]	Potassium ferrocyanide	100	100	6.2	55	3.2	2	87
43-4[d]	Potassium ferrocyanide	100	100	6.2	55	3.3	2	87
43-5[d]	Potassium ferrocyanide	100	100	6.2	55	4.6	2	87
47-1[e]	Synthetic waste	88	100	11.4	55	--	2	98
47-2[e]	Synthetic waste	88	100	7.0	55	5.5	6	93
47-4[e]	Synthetic waste	88	100	6.0	55	5.0	15	83
47-5[e]	Synthetic waste	88	100	4.0	55	3.1	43	51

(a) Aliquat 336 solution used contained 95 ml of the liquid reagent, 72 ml of isodecanol dissolved in kerosene and diluted with kerosene to 1 liter. The solution is 0.05 M with respect to reagent concentration.

(b) This run was made using the organic phase from 48-1 as the extractant. This material contained 113 ppm of cyanide.

(c) Sodium ferrocyanide formed by adding ferrous sulfate to sodium cyanide solution.

(d) Reagent grade.

(e) Synthesized waste solution contained 88 ppm cyanide, 12 ppm nickel, 12 ppm zinc, 14 ppm copper, 5 ppm cadmium, and 12 ppm iron.

TABLE 10. MIXER-SETTLER EXPERIMENTS ON CYANIDE SOLUTIONS USING ALIQUAT 336

Expt. No.	Feed Solution			Feed Rate, ml/min	Duration of Run, min	Organic Feed Rate, ml/min	End Solution	Extraction, percent
	Type	ppm CN	pH				ppm CN	
81	Zinc Cyanide[a]	100	7	200	210	20	9.7-13.0	87-92
75-76	Zinc Cyanide[a]	100	10	200	210	20[c]	<1-5	95-99+
82	Copper Cyanide[b]	100	10	200	210	20	<1-6.5	93-99+

(a) Solution fed contained 100 ppm cyanide; 53 ppm zinc.

(b) Solution fed contained 100 ppm cyanide; 82 ppm copper.

(c) Trichloroetnane used as solvent instead of kerosene in this run.

that cyanide probably could be reduced to the desired level of less than 1 ppm consistently, the laboratory work failed to demonstrate this.

The results of studies on the reagent regeneration by stripping also indicated that this was a problem. In no case was adequate stripping of cyanide from "loaded organic solution" satisfactorily achieved. It is believed that a more intensive and systematic campaign would be necessary to evaluate fully the feasibility of stripping cyanide or cyanide complexes from the organic solutions.

Studies on Acidification and Volatilization of Cyanide

Acidification-aeration as a means for eliminating cyanide from metal-finishing wastes once was practiced commercially. Reportedly, the process is no longer being used. In the commercial process the waste was acidified, heated, and then swept with large volumes of air to eliminate the cyanide as hydrogen cyanide gas. The gas was discharged up a stack and presumably was sufficiently dispersed so as to be harmless. The suitability of such a process for the smaller plater likely to be located in heavily populated areas and subject to local government restrictions seems dubious. However, a variation of this process that might fit the requirements of smaller establishments was conceived and tested in a very preliminary fashion during this program. The envisaged process is depicted in Figure 6.

The process would consist of passing the slightly acidified and possibly heated waste through a vacuum system. The exhaust from a mechanical vacuum pump would be introduced into a sodium hydroxide absorbing solution which would readily absorb the cyanide gas and whatever CO_2 was exhausted by the pump. Alternately, the exhaust from the vacuum pump could be directed to a flare which would destroy cyanide by combustion. Periodically some or all of the loaded absorbent would be removed and fresh sodium hydroxide solution added. The spent solution either could be treated by a conventional destruction method or could be sent to a recovery step. Depending on the carbon dioxide content of the exhaust gases, various amounts of sodium carbonate would be present in the absorbent solution along with sodium cyanide. If too much were present for reuse of the cyanide solution in plating, it might be treated with calcium cyanide to precipitate calcium carbonate and to form sodium cyanide according to the reactions:

Na_2CO_3	+	$Ca(CN)_2$	→	2NaCN	+	$CaCO_3$.
Sodium carbonate		Calcium cyanide		Sodium cyanide		Calcium carbonate precipitate

A process of this type, if workable, would eliminate the shortcomings of simple acidification aeration such as:

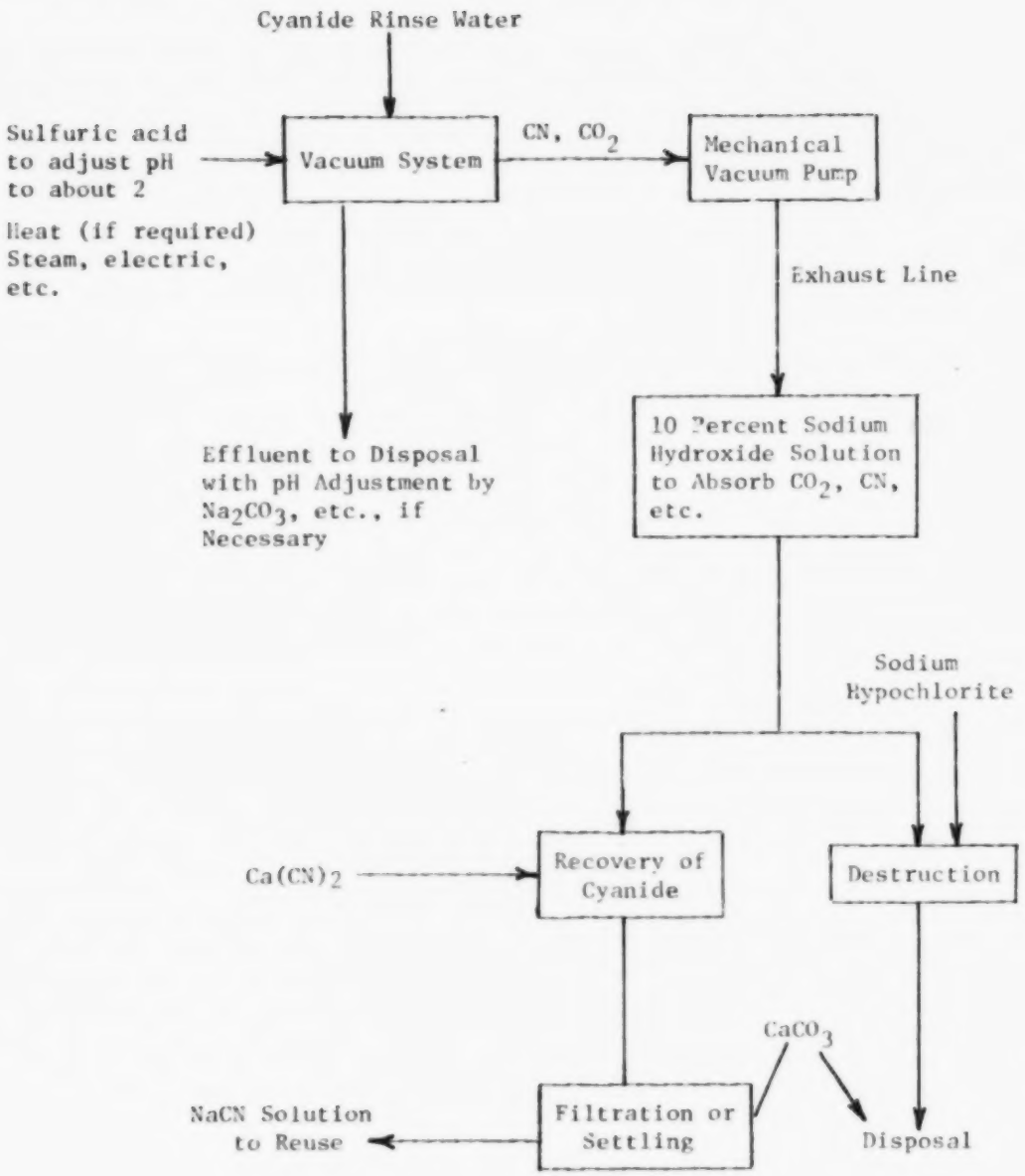

FIGURE 6. SPECULATIVE ACIDIFICATION- VOLATILIZATION PROCESS FOR CYANIDE WASTES

(1) The discharge of cyanide to the atmosphere

(2) The use of large quantities of air which would make absorption and hence recovery of cyanide difficult if not impossible.

The technical feasibility of this type of process was investigated on a batch scale using sodium cyanide solutions and, in other experiments, solutions containing complex metal cyanides. In these experiments, solutions of cyanide were acidified to a pH of 3, transferred to a glass filter flask, heated to about 100 F, and maintained at that temperature throughout the run during which they were stirred mechanically. A vacuum of about 25 to 28 inches of mercury was applied. Samples were removed at various intervals of time and analyzed for cyanide.

The data developed during this series of experiments are summarized in Table 11. As shown the percentage of cyanide that was volatilized varied considerably, depending on the time for evacuation, the concentration, and the type or form of cyanide in the solution. At a concentration of about 50 ppm cyanide, good removals (greater than 95 percent) were obtained after 30 minutes from solutions containing free cyanide (sodium cyanide) or from solutions containing the weaker cyanide complexes (zinc and cadmium cyanides). The percentage removals decreased slightly to about 92 percent in 30 minutes for solutions containing 260 ppm cyanide in these same forms. For solutions containing either copper or nickel, however, much lower removals were observed, indicating that these metals form stronger complexes with cyanide and would require a much longer treatment time to reduce cyanide to an acceptable level.

On the basis of these experiments, it was concluded that the process is technically feasible at pH = 3 for most of the major types of plating rinse waters (zinc, cadmium, and free cyanide solutions). If copper or nickel (and probably iron) is present, the method would be prohibitively long and for all practical purposes not feasible for the smaller plater.

Activated Carbon Adsorption Studies

General Description of Method. During the search of the literature for the state-of-the-art review, references were found in which the use of activated carbon for the adsorption of chromium from solution was cited. Activated carbon has been studied by various investigators for the tertiary treatment of domestic wastewaters. It also has been used for the adsorption of various materials from solution, including metal ions. For these reasons it was concluded that adsorption on activated carbon should be one of the techniques to be evaluated during this phase of the program.

Modern theories hold that the adsorption of materials from solution by activated carbon is accomplished by van der Waal or dispersion forces. These forces exist among all molecules and atoms, whether or not they are

TABLE 11. REMOVAL OF HCN FROM COMPLEX CYANIDES BY ACIDIFICATION-VOLATILIZATION AT pH 3

Type of Solution(a)	Evacuation Time, min	Cyanide Removed, mg	Residual Cyanide, mg	Apparent Percent Removal
Sodium Cyanide (52 ppm CN)	15	46.0	--	87
	30	52.5	0.2	99.6
Sodium Cyanide (260 ppm CN)	15	197.4	--	80
	30	229.8	18.5	93
Zinc Cyanide (52 ppm CN)	15	45.5	--	89
	30	50.0	1.0	98
Cadmium Cyanide (52 ppm CN)	15	40.6	--	79
	30	49.1	2.6	95
Cuprous Cyanide (52 ppm CN)	15	31.7	--	67
	30	37.1	10.2	78
Cupric Cyanide (52 ppm CN)	15	27.9	--	66
	30	31.1	11.4	73
Nickel Cyanide (52 ppm CN)	15	11.3	--	24
	30	20.2	26.8	43
Mixed Cyanides (260 ppm CN)	15	187.4	--	80
	30	213.6	20.6	91

(a) Initial solutions were made up to 1 liter and maintained at 100 F during evacuation.

chemically combined, and may be considered analogous to the gravitational force the earth exerts upon objects near it.

The ability of activated carbon to adsorb a given material depends largely on its surface area. Each particle of activated carbon has a vast interconnecting network of many-sized pores, providing a very large surface area for adsorption. Consequently, the pore structure of activated carbons is extremely important in determining their adsorptive properties.

Although the reasons are not completely understood, it is known that other substances have an influence on the adsorptive properties of activated carbons. Oxygen combined with the carbon can be particularly important and can increase its affinity for polar compounds and decrease its affinity for nonpolar compounds. In some cases, the inorganic-ash portion of the carbon can also influence the adsorption process. These latter factors may play a major role in the adsorption of inorganic materials.

Activated carbons are usually classified according to their physical form (e.g., powdered or granular) and according to their use (e.g., water grade, decolorizing, liquid phase, or gas phase). Granular carbons are those materials which are over 150 mesh in particle size and powdered carbons are those which are smaller in particle size.

Activated carbons are produced from various carbonaceous raw materials (e.g., bituminous coal, nut shells, lignite, pulp-mill residue, and wood). During this experimental program, many types and sizes of activated carbon were studied for the removal of chromium from waste solutions.

Equipment and Procedure. In preliminary batch experiments on the adsorption of cyanide, various amounts of carbon were mixed with a synthetic cyanide waste solution and the mixture was stirred for a predetermined time at room temperature. The mixture then was filtered on glass filter paper and the filtrate analyzed for total cyanide.

During the preliminary experiments, several sizes of activated carbon, as well as those produced from various materials, were evaluated. The carbons studied are listed in Table 12.

In subsequent continuous-adsorption experiments, a series of four glass columns, arranged as shown in Figure 7, was employed. The columns were constructed of 2-inch-diameter Pyrex glass tubing and were approximately 30 inches in length. By pumping the solution through the four columns in series, a total carbon bed depth of 10 feet was attainable. The granular carbon was supported on a 65-mesh stainless steel grid. Oscillating pumps were used to pump the solution down through the columns. The columns were constructed with a sampling port at the bottom of each one so that effluent samples could be obtained for analysis. The type carbon selected for the continuous experiments was Pittsburgh Activated Carbon.

TABLE 12. TYPES OF ACTIVATED CARBON BEING EVALUATED

Trade Name	Company	Source Material	Type and/or Size
Nuchar	West Va. Pulp & Paper	Pulp mill residue	Granular (8 x 30) (WVL)
"	ditto	ditto	Pulverized
Pittsburgh	Pittsburgh Act. Carbon Co.	Bituminous coal	Pulverized (RC)
"	ditto	ditto	8 x 30 (SGL)
"	"	"	12 x 40 (CAL)
"	"	"	20 x 50 (OL)
Absorbite	Barneby-Cheney	Nut shells	Pulverized, nonactive (XB)
"	ditto	ditto	Granular, nonactive (BB)
"	"	"	Pulverized, low-active (YD)
"	"	"	Granular, low-active, 12x30 (PA)
"	"	"	Pulverized, high-active (XZ)
"	"	"	Granular, high-active, 10x50 (PC)
"	"	"	Pulverized, acid wash (JF)
"	"	"	Granular, acid wash, 10x50 (PK)
Cliffchar	Royal Oak Charcoal Co.	Wood charcoal	Pulverized
"	ditto	ditto	Granular, 10 x 20

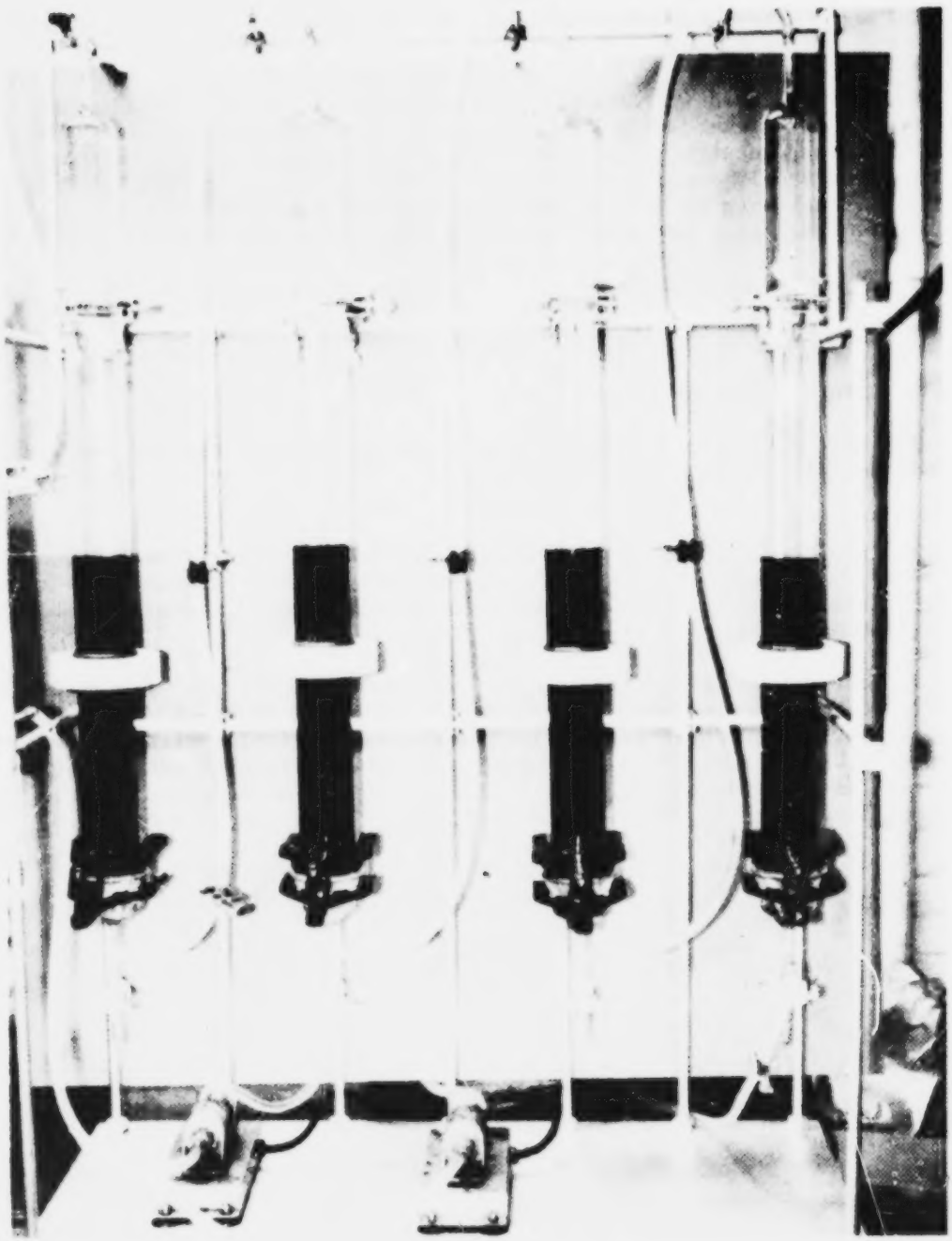

FIGURE 7. BENCH-SCALE CONTINUOUS COLUMNS FOR ADSORPTION EXPERIMENTS

Company's Type OL which is a granular carbon with a particle size of 20 x 50 mesh. This selection was based on the overall results of preliminary batch experiments.

The procedure used in the continuous experiments was to pump a synthetic waste solution containing varying amounts of cyanide through the column at a given rate with periodic analysis of effluent samples. In most experiments only one column was used so that the time of "breakthrough" could be observed as well as the time when the carbon was completely loaded. The major variables studied during these experiments were:

(1) pH of the feed solution

(2) Concentration of the feed solution

(3) Rate of flow or residence time

(4) Ionic form of the element in solution (e.g., free cyanide, complexed cyanide, or cyanide/chromium mixtures).

Results of Preliminary Batch Studies. The initial experimentation on the removal of cyanides by adsorption on activated carbon was carried out on solutions made from distilled water and sodium cyanide containing 100 ppm of cyanide.

The first series of experiments was concerned with a study of the effect of pH on cyanide removal. The pH value was varied by the addition of either dilute sulfuric acid or sodium hydroxide solution prior to contacting with the carbon. The conditions and results obtained from this series of experiments are shown in Table 13. It can be seen that maximum removal amounted to only about 50 percent at pH values of 8 or below.

TABLE 13. EFFECT OF pH ON THE REMOVAL OF CYANIDE WITH ACTIVATED CARBON

pH	Cyanide Removal, percent
12	9
10(a)	18
8	50
6	48
4	50
2	50
1	45

(a) No acid or caustic required to obtain pH 10 since this is normal value of 100 ppm cyanide.

Conditions: Aqua Nuchar A carbon; carbon concentration, 5 g/l; contact time, 5 minutes; agitated by stirring in an open beaker.

Another series of experiments was run to determine the effect of contact time on cyanide removal. Conditions and results are shown in Table 14. The results showed that increasing the contact time from 5 to 40 minutes increased the percentage of removal from 50 to 98. Longer contact time did not increase the percentage of cyanide removal.

TABLE 14. EFFECT OF CARBON CONTACT TIME ON CYANIDE REMOVAL

Contact Time, minutes	Cyanide Removal, percent
5	50
10	65
20	88
40	98
60	98

Conditions: Aqua Nuchar A Carbon; carbon concentration, 5 g/l; pH 2.0; agitated by stirring in an open beaker.

It was found that significant amounts of cyanide were being evolved as HCN rather than being adsorbed at the low pH values. Several tests were made to determine the relative amount of cyanide that was volatilized and so not adsorbed. Sodium cyanide solutions containing 100 ppm of cyanide were stirred for various time periods without carbon addition. One sample was stirred at pH 2 and another sample at pH 10 (the normal pH value of the sodium cyanide). The results are shown in Figure 8. A large percentage of cyanide was evolved from the low pH solution even after only 10 minutes of stirring while the solution at pH 10 did not lose a significant amount of cyanide until after 10 minutes. This observed loss at the high pH value may have been due to oxidation rather than volatilization. However, at both pH levels the amount of cyanide increased with increased stirring time. In view of these results, it was decided that the preceding experiments probably did not show actual adsorption characteristics and that an alternative procedure would be needed to prevent cyanide losses by volatilization.

Subsequent experiments using an alternate procedure were conducted to determine which of the various types of carbon (listed previously) were more suitable for cyanide adsorption. For these experiments, the activated carbon and the solution were agitated by rolling in a sealed jar to prevent oxidation of the cyanide or its loss by volatilization. The mixtures were then filtered after the desired time had elapsed and the filtrate analyzed. These experiments were run on pure sodium cyanide solutions. The conditions and results are shown in Table 15. These data indicate that the Pittsburgh carbon gave better overall performance than the other types used. The percentage removal of cyanide

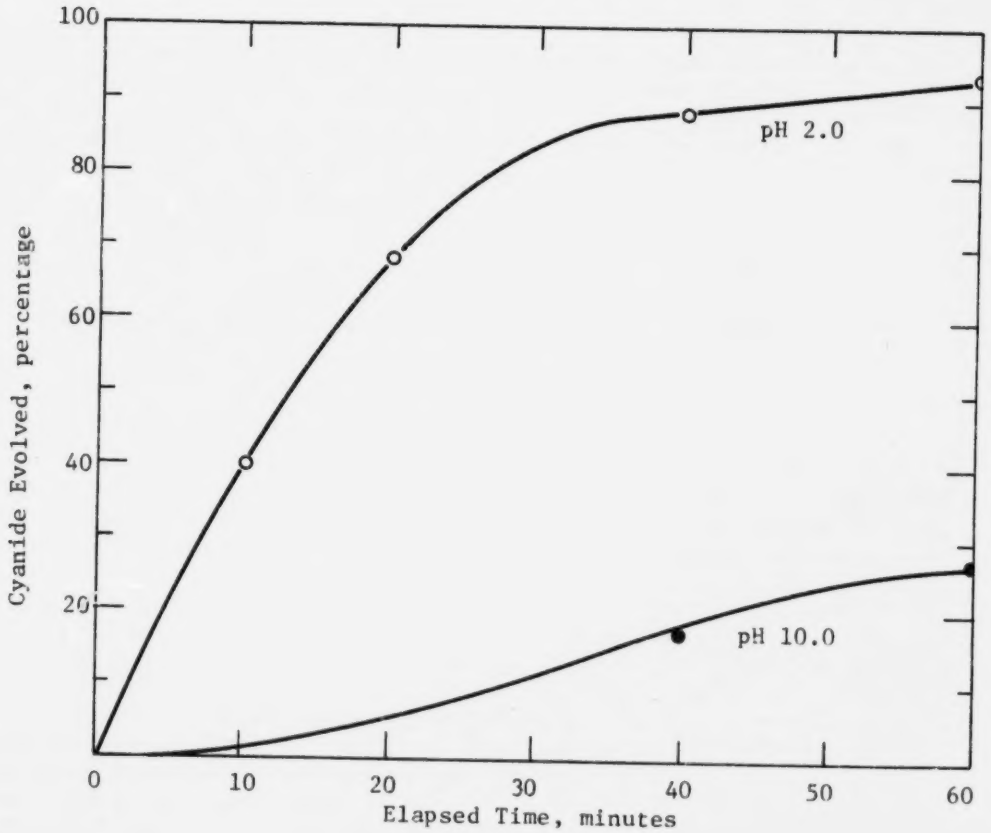

FIGURE 8. EFFECT OF STIRRING TIME ON CYANIDE EVOLUTION

TABLE 15. AMOUNTS OF CONTAMINANT REMOVED IN BATCH EXPERIMENTS USING VARIOUS ACTIVATED CARBONS[a]

Type of Activated Carbon	Removal, percent		
	Cyanide[b]	Mixture[c]	
		Chromium	Cyanide
Nuchar, pulverized (pulp mill residue)	35	41	53
Nuchar, granular (pulp mill residue)	38	48	45
Pittsburgh, pulverized (bituminous coal)	33	60	65
Pittsburgh, granular (bituminous coal)	35	60	58
Absorbite, pulverized (nut shell)	25	6	58
Absorbite, granular (nut shell)	20	3	25
Cliffchar, pulverized (wood charcoal)	30	--	38
Cliffchar, granular (wood charcoal)	27	6	40

(a) Conditions: Carbon concentration: 10 g/l
Contact time: 10 minutes
Agitation: Rolling in sealed jar.

(b) Starting solution contained 100 ppm cyanide added as sodium cyanide; pH 10.

(c) Starting solution contained 10 ppm chromium and 10 ppm cyanide added as potassium dichromate and sodium cyanide; pH 5.9.

from the mixed solution was higher, in all cases, than that from the pure cyanide solution. Because different levels of cyanide were involved (10 and 100 ppm, respectively) and because two different pH levels were employed (5.9 and 10), it cannot be stated positively that the mixed waste responded better. It does suggest the possibility that the presence of chromium may have assisted in removing some cyanide.

Several series of experiments also were conducted with complex cyanides of cadmium and nickel. In the first series, the solution contained 36 ppm cadmium and 64 ppm cyanide, and the activated carbon concentration was varied from 5 to 40 grams per liter. Contact time was held constant at 5 minutes at pH = 9.6. The results of these experiments are shown in Figure 9. They indicate that carbon concentrations of 25 grams per liter and higher effected a maximum of about 90 percent cyanide removal.

In another series of experiments, a solution containing 56.4 ppm nickel and 100 ppm cyanide was treated under conditions similar to those used for cadmium cyanide, except that the pH was held at 7.0. The results of this series shown in Figure 10 indicate that 30 grams per liter of carbon gave almost complete removal of cyanide.

On the basis of the results obtained in these preliminary batch experiments, only tentative conclusions could be drawn:

(1) The adsorption of uncomplexed cyanide (free cyanide) by activated carbon probably does not occur to an appreciable extent, although some adsorption apparently takes place at the lower pH levels. The magnitude of the adsorption is difficult to pinpoint, owing to uncertainty about the extent that volatilization, oxidation, or other unknown processes may be occurring.

(2) The complexing of the cyanide with metals such as nickel and cadmium (and iron, zinc, and copper) enhances the adsorptive power. The experimental results suggested that the nickel complex adsorbs completely and rapidly and the cadmium complex somewhat less completely and only under specific conditions of pH and carbon concentration. More laboratory work would be required to determine whether a practical process based on cyanide complexation-adsorption is feasible.

(3) Certain carbons appear to be superior to the other carbons tested.

Studies on Formation of Complex Metal Cyanides. On the basis of the preliminary studies just described, it was concluded that the development of a workable process for cyanide removal probably depended on the use of metal cyanide complexes rather than free cyanides. It also was evident that more basic information was needed above that appearing in the literature on the formation, behavior, and properties of metal cyanide complexes as produced in or from electroplating rinse waters. A brief study therefore was undertaken to provide this information.

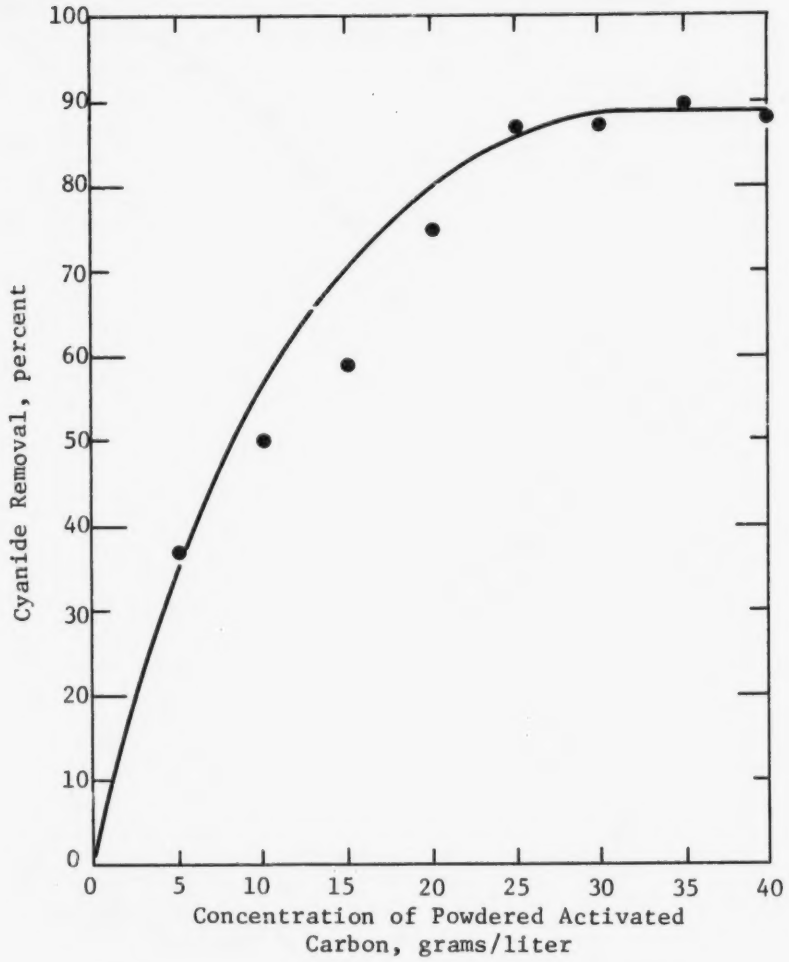

FIGURE 9. EFFECT OF POWDERED ACTIVATED CARBON ON THE REMOVAL OF CYANIDE FROM A SOLUTION CONTAINING CADMIUM CYANIDE

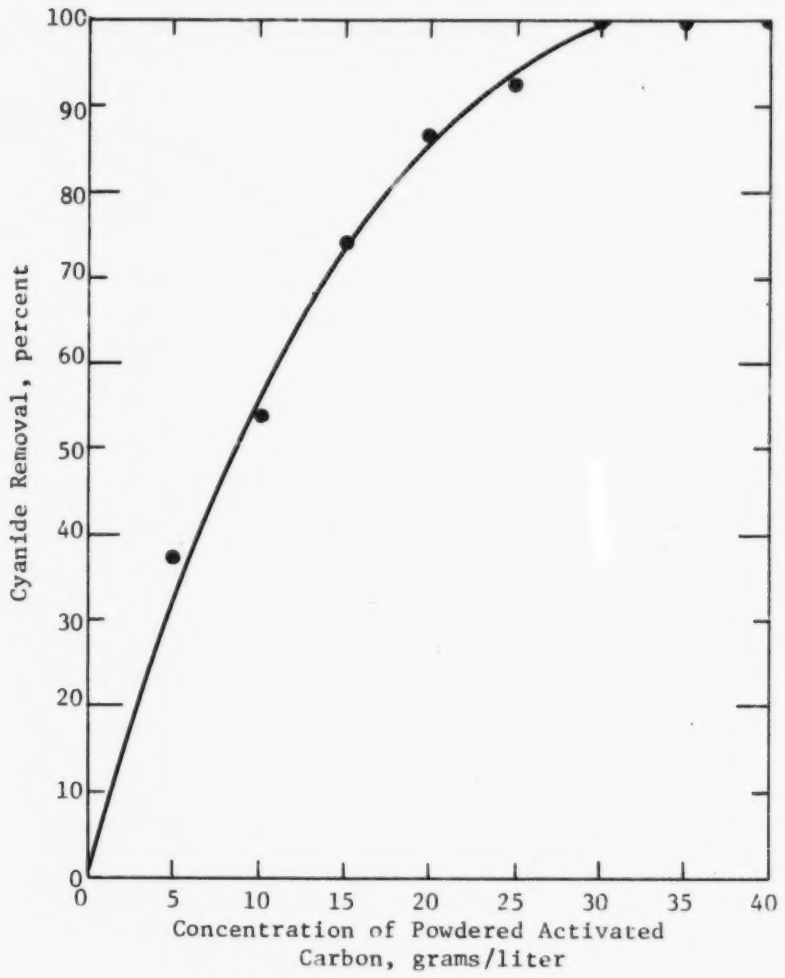

FIGURE 10. EFFECT OF POWDERED ACTIVATED CARBON ON THE REMOVAL OF CYANIDE FROM A SOLUTION CONTAINING NICKEL CYANIDE

The emphasis in this work was to develop conditions and procedures for the formation of specific complex cyanides (e.g., iron, zinc, copper, nickel) which then might be effectively removed by one or more of the removal techniques under consideration such as carbon adsorption or ion flotation.

The experiments in this study were conducted with the aid of an Orion Model 401 specific ion analyzer using electrodes for measuring free cyanide in aqueous solutions. This instrument indicates the free cyanide concentration in a range of 0.01 to 100 ppm but does not apparently indicate cyanide which is bound in a metal complex or cyanide present as HCN. This characteristic provided a convenient method for studying the rate of complex formation under various experimental conditions.

Typical data which were obtained initially on the complexing of cyanide with four different metals are shown in Figures 11 and 12. The data in Figure 11 illustrate the rate of complexing with each metal in 0.1 molar NaOH solution (pH = 12). As shown, the free cyanide concentration decreased with time after the addition of stoichiometric amounts of the various metals added as sulfates to sodium cyanide solutions. For zinc, copper, and nickel, a stoichiometric ratio of 4 parts cyanide to 1 part metal was selected. For iron, a ratio of 6:1 was selected. For the runs with iron, zinc, and copper, the amounts of metal were doubled after 15 minutes had elapsed during complexing. In the case of nickel, only a 20 percent excess of this metal was subsequently added after 30 minutes had elapsed.

The results shown in Figure 11 illustrate the marked difference observed in complexing ability between the individual metals. Nickel, for example, exhibited a rapid and complete reaction in that free cyanide was reduced to less than 1 ppm in 3 minutes and to less than 0.2 ppm in 40 minutes. Copper was the second most effective reagent and reduced free cyanide to about 1.5 ppm in 60 minutes. By contrast, the reactions with iron and zinc were exceedingly slow; only about 50 percent of the free cyanide was complexed in 60 minutes.

The results obtained with zinc, copper, and nickel were expected since these metals form progressively more stable complexes with cyanide and thus should show more complete reaction proceeding from zinc to copper to nickel. However, since iron is known to form very stable complexes similar to that of nickel, the very slow and incomplete reaction observed above was somewhat unexpected. In order to further investigate this aspect, a subsequent series of runs was made with iron at various pH levels. In these experiments, solutions containing 100 ppm cyanide were maintained at constant pH values (7.0, 8.0, 9.0, 10.0, and 11.0) and incremental amounts of ferrous sulfate corresponding to 0.4 to 2.0 times the theoretical amount were added. The solutions were agitated for 10 minutes after each addition of ferrous sulfate. Samples were then taken and diluted by a factor of 10 with 0.1 molar NaOH to allow direct measurement by the specific ion meter. Figure 12 presents the data which were obtained from this series of experiments. As shown, changes in pH produced

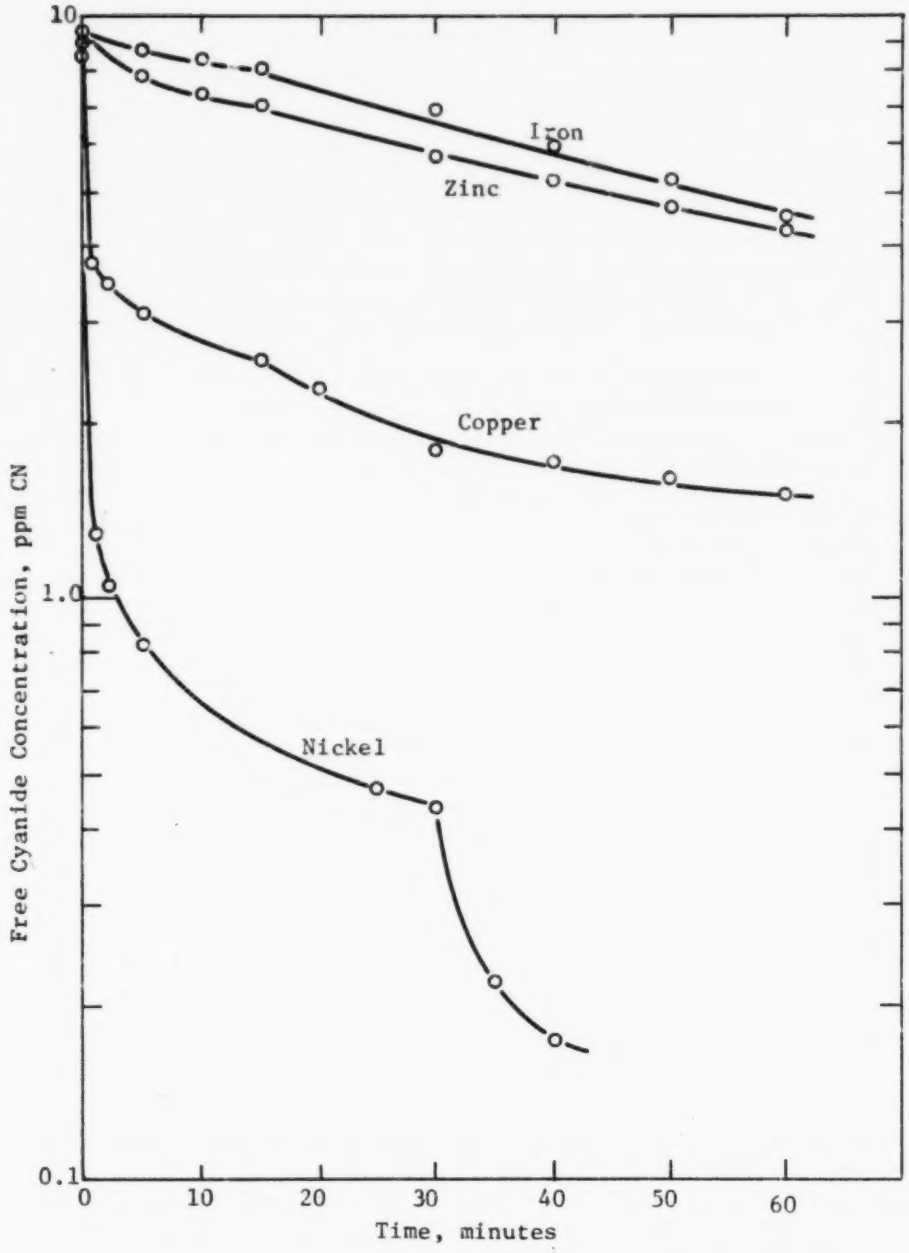

FIGURE 11. RATE OF COMPLEX CYANIDE FORMATION WITH VARIOUS METALS

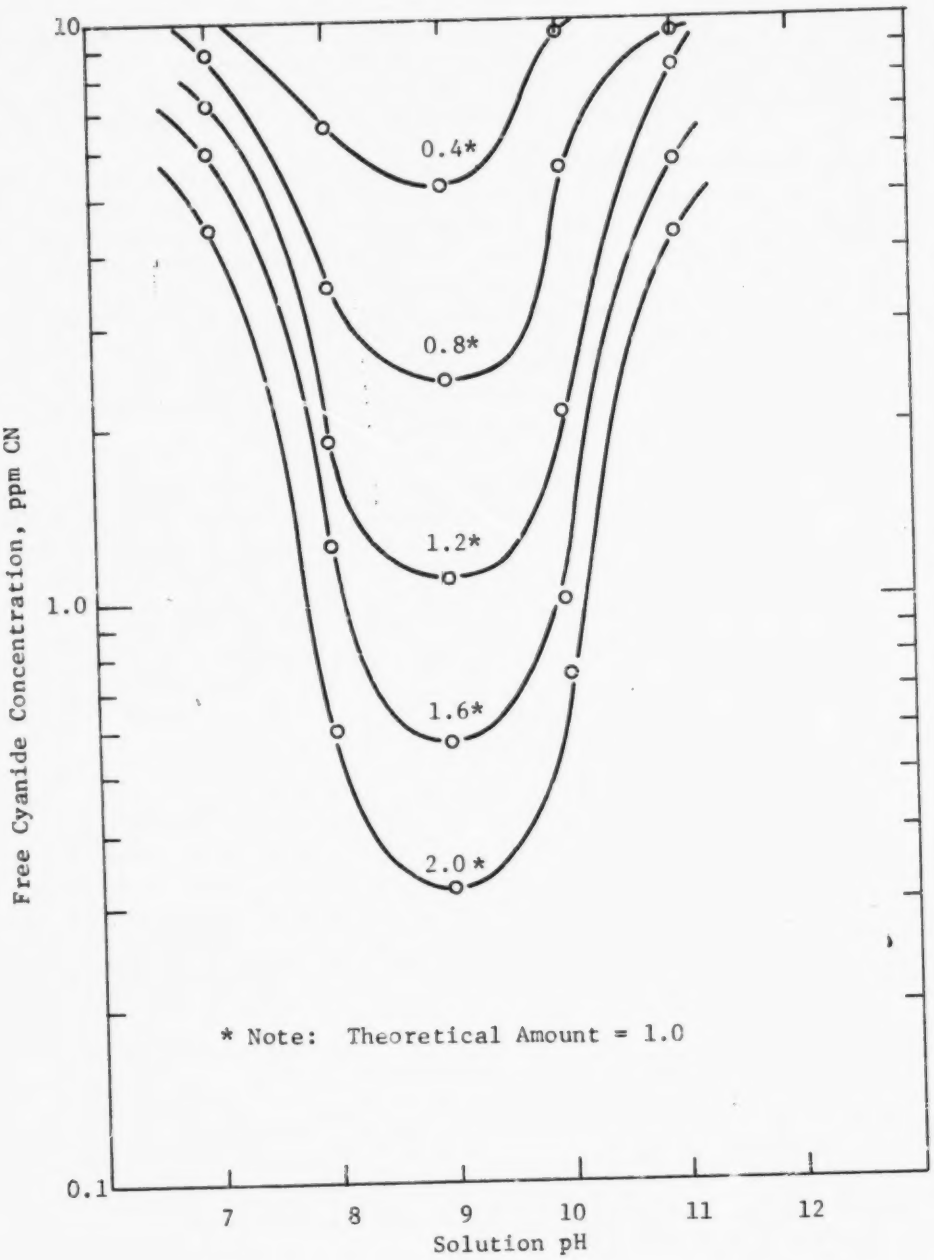

FIGURE 12. EFFECT OF pH ON COMPLEX CYANIDE FORMATION WITH ADDITION OF FERROUS SULFATE

a marked effect on the extent of the complexing reaction. Also evident is the effect of excess ferrous sulfate in increasing the amount of complex formed. The data explain the very slow reaction at pH 12 observed initially and indicate that a close control of pH and concentration is important to provide maximum formation of complex iron cyanides.

Although the above data indicated that optimum formation of iron cyanides could be effected under certain conditions, the results were found applicable only to simple cyanide solutions containing sodium cyanide. During subsequent experiments, the investigation was extended to include more representative waste cyanide solutions which would contain cyanide already partially complexed with metals such as zinc or cadmium. It was found that the presence of these metals, which form mild complexes with cyanide, greatly interfered in some cases with the formation of the stronger complexes such as those of nickel, copper, and iron. Typical data showing this effect are given in Tables 16, 17, and 18.

In Table 16, data are shown for the residual free cyanide concentration remaining at various time intervals after addition of zinc sulfate, followed by the addition of ferrous sulfate. The amount of zinc added was equal to the theoretical amount (4 parts cyanide to 1 part zinc) for complete formation of the complex. Iron additions corresponded to 5 times the theoretical amount for complete complex formation. In Tables 17 and 18 comparative data are shown for additions of zinc sulfate followed by either copper or nickel sulfate except that the amount of nickel added was only 1.1 times the theoretical amount and the amount of copper added was 1.5 times the theoretical amount.

The three sets of data suggest a clearcut difference in the complexing ability of iron versus nickel and copper. With iron--even at 5 times the theoretical amount--complex formation was greatly retarded by the previous addition of zinc to the solution. The reaction with nickel--at 1.1 times the theoretical amount--was only slightly affected by zinc. This occurred at all pH values investigated with a pH of 10 being optimum for greatest formation of the cyanide complex of either metal. Similar data also were obtained when cadmium was used in place of zinc as the interfering metal.

On the basis of the results of these experiments, it was concluded that:

(1) Nickel and copper probably are the best complexing agents for free cyanide and also for cyanide that has been previously complexed with zinc or cadmium and might be incorporated into a removal process using either ion flotation or carbon adsorption. Economics considerations suggest that wastes generated within the plant would be required to provide sources of these metals.

(2) The use of iron for complex formation and subsequent removal of the cyanide does not appear feasible. The results indicate that good complex formation with iron occurs only by careful control of the solution pH and with simple cyanide solutions containing free cyanide. The experiments with more representative waste cyanide solutions containing

TABLE 16. EXPERIMENTAL DATA ON COMPLEX CYANIDE FORMATION WITH ADDITIONS OF ZINC SULFATE FOLLOWED BY FERROUS SULFATE

Elapsed Time, min	Free Cyanide Concentration, ppm CN				
	pH 9	pH 9.5	pH 10	pH 10.5	pH 11
0	10.0	10.0	10.0	10.0	10.0
1	7.0	5.8	4.4	6.5	8.0
2	6.8	5.7	4.2	6.3	8.0
5	6.2	5.4	3.9	5.8	8.0
10	6.2	5.3	3.7	5.4	7.6
20	5.8	4.8	3.4	4.8	7.0
30	5.5	4.4	3.2	4.5	6.6

TABLE 17. EXPERIMENTAL DATA ON COMPLEX CYANIDE FORMATION WITH ADDITIONS OF ZINC SULFATE FOLLOWED BY NICKEL SULFATE

Elapsed Time, min	Free Cyanide Concentration, ppm CN			
	pH 9	pH 10	pH 11	pH 12
0	10.0	10.0	10.0	10.0
1	0.27	<0.1	2.2	3.8
2	0.17	<0.1	2.0	2.7
5	<0.1	<0.1	1.7	1.9
10	<0.1	<0.1	1.4	1.3
20	<0.1	<0.1	1.2	0.9
30	<0.1	<0.1	1.1	0.6

TABLE 18. EXPERIMENTAL DATA ON COMPLEX CYANIDE FORMATION WITH ADDITIONS OF ZINC SULFATE FOLLOWED BY COPPER SULFATE

Elapsed Time, min	Free Cyanide Concentration, ppm CN			
	pH 9	pH 10	pH 11	pH 12
0	10.0	10.0	10.0	10.0
1	1.0	0.5	0.9	3.7
2	1.1	0.5	0.8	3.3
5	1.6	0.5	0.8	5.0
10	1.6	0.5	0.7	2.8
20	1.5	0.5	0.7	2.6
30	1.4	0.5	0.7	2.5

zinc or cadmium indicate that these metals seriously interfere with subsequent complexing by iron.

Continuous Column Adsorption Studies. The results of previous work on the adsorption of cyanide by activated carbon indicated that complexation of the cyanide by certain metals very probably would be required for virtually complete adsorption and adequate capacity of the carbon. Early experiments made during the first phase of this project showed that free cyanide and the relatively weak zinc cyanide were very incompletely adsorbed and that the capacity of the carbon was too low. They also showed that carbon adsorption of ferrocyanide offered some promise. In those experiments, up to 95 percent of the cyanide (in the ferrocyanide form) was adsorbed in the continuous carbon column. Although no adsorption studies were made on copper or nickel cyanides in the belief that if iron could be made to work, the others would be a poor economic competitor, it was believed that complex copper or nickel cyanides might be adsorbed as readily as ferrocyanide.

A more basic study of the requirements for complexing was undertaken, the results of which indicated that the presence of other metals (such as zinc, which would normally occur in plating rinse waters) seriously affects complexation by ferrous iron (Table 16). Accordingly, the plans for carbon adsorption experiments on the ferrocyanide system were abandoned. On the other hand, the presence of zinc was shown not to interfere with the formation of complex copper or nickel cyanides (Tables 17 and 18).

Parallel to the complexation studies described in the previous section, several continuous experiments were made to fill in a gap in the existing data on adsorption. Continuous experiments had been made on free cyanide, zinc cyanide, and ferrocyanide, but no data had been developed for the copper cyanide system itself. The purpose of the experiments described below was to determine the behavior of the copper cyanide system in the adsorption process.

Studies on the copper cyanide system. Two experiments were made concurrently by separate investigators to accelerate the work. One experiment was carried out in the apparatus shown in Figure 7 and by the general procedures described previously. This run was made on a solution containing 100 ppm each of cyanide and copper preadjusted to pH 10.

The second experiment was done in a 1-1/2-inch-diameter glass column containing 100 grams of activated carbon, with arrangement for continuously feeding solution through a large separatory funnel. It was made on a feed containing 50 ppm of cyanide and 64 ppm of copper at pH 3.0. At this pH a white salt, presumably cuprous cyanide [$Cu(CN)_2$] was precipitated.

The feed rates employed in each experiment were reasonably proportionate to the volume of carbon involved in each case. In the experiment run in the 2-1/2-foot column which contained 700 grams of activated carbon, the

overall feed rate which held fairly constant throughout the run was about 450 ml per minute. The initial feed rate in the second experiment made with 100 grams of carbon was 70 ml per minute. The precipitated $Cu(CN)_2$, however, which collected on top of the bed, slowed the feed rate to about 40 ml per minute after several hours of operation. When this precipitate was removed the original feed rate was restored. Both experiments were begun with fresh carbon and were continued until the effluents approached closely to the pH values of the original feed solution. During each experiment, effluent solutions were periodically analyzed for cyanide, copper (qualitatively), and pH values.

Cyanide adsorption in the run made on the solution containing 100 ppm of cyanide and copper at pH 10 was initially good. Effluents for the first 24 hours of operation contained from 1 to 2 ppm of cyanide, equivalent to 98 to 99 percent removal. After this period, however, the cyanide content of the effluent gradually mounted to about 4 ppm after 3 hours and 12 ppm after 4 hours, holding at that level for 2 additional hours.

In the experiment made at pH 3 on the solution containing 52 ppm of cyanide and 64 ppm of copper, almost complete removal of cyanide was obtained in the first half hour, but thereafter rose to 3-4 ppm after 1 hour. It remained at this level for an additional hour and then dropped to about 1.5 ppm when the feed rate was decreased to about 40 ml/minute by the formation of a precipitate on top of the carbon bed. When the precipitate was removed and the normal flow reestablished, the cyanide content of the effluent quickly rose to 5-6 ppm.

The data from the experiment at pH 10 were promising. In this run about 70 liters of solution containing 100 ppm of cyanide was passed through 700 grams of carbon with about 98 percent removal of cyanide. The indicated capacity of the carbon for cyanide, about 1.1 percent, was considerably greater than has been obtained in any previous experiments. Operation with a feed at pH 3 did not appear as promising because the degree of cyanide removal was not as great, and the precipitate of $Cu(CN)_2$ which forms at this pH would tend to plug the column.

Although the results obtained in these preliminary runs were promising, several unknown factors remained to be investigated before the feasibility of the technique could be confirmed. These included:

(1) The effect of pH on adsorption. In the experiment made at pH 10, maximum adsorption (98 percent) was obtained when the effluent pH was about 7. As the effluent in this experiment approached 10, adsorption decreased. In the experiment made with the feed at pH 3 such a pattern was not observed and the poorest adsorption occurred with effluents of about pH 7.

(2) The regeneration of the carbon after loading could be difficult. After the adsorption experiments, attempts were made to regenerate the carbon with strong caustic. During regeneration copper removal was found to be only about 50 percent complete by this means and yielded

solutions containing only about 1.3 grams per liter of copper. The remainder of the copper was readily removed from the carbon with 10 percent nitric acid.

In subsequent experiments, the emphasis was to investigate the effect of pH values intermediate between 3 and 10. It was found that at pH values between 3 and 6, the process was complicated by the presence of precipitated $Cu(CN)_2$. Although good adsorption was obtained, the column tended to become clogged and the required flow rate of feed solution could not be maintained. At higher pH values of 10, the operation also was affected by the presence of precipitated solids, either zinc hydroxide or copper hydroxide--the latter coming from the use of excess copper during complexation. Both of these conditions were not consistent with a practical process in the downflow mode of operation.

An evaluation of cyanide adsorption at pH 7 then was conducted using the continuous column apparatus. The adsorption experiment was begun with a feed solution containing 104 ppm total CN, 66 ppm zinc, and 95 ppm cupric copper. The solution was initially adjusted to a pH of 10 with sodium hydroxide to provide maximum complexing of the copper and cyanide. After agitating for 5 to 10 minutes, the solution was adjusted to pH 7 with sulfuric acid for the adsorption cycle. Previous experiments on complex formation indicated that the copper complex forms readily under these conditions and results in a solution containing less than about 3.5 ppm cyanide as free cyanide. The remaining cyanide was believed to react with cupric copper according to the following equation:

$$2Cu^{+2} + 2OH^- + 7CN^- \rightarrow 2Cu(CN)_3^{-2} + CNO^- + H_2O.$$

The presence of cyanate definitely was established in the feed and effluent solutions used during this experiment. The results of chemical analysis showed about 26 ppm cyanate in both the feed and effluent samples indicating essentially no adsorption of this component.

During the adsorption cycle, the carbon column was operated with a feed rate of between 300 and 400 cc/minute over a period of 11 days. A total of about 275 gallons of solution was fed to the column. Experimental data obtained as the run progressed are shown in Table 19.

The results obtained during the experiment were encouraging. Cyanide removal initially was greater than 99 percent and gradually decreased to about 85 percent near the end of the experiment. The operation was discontinued when the level of cyanide in the effluent increased above 10 ppm of cyanide.

For the entire experiment, a total of about 70 grams of cyanide was adsorbed on the 700 grams of carbon contained in the column. Approximately 30 grams of cyanide were converted to cyanate and not adsorbed by the carbon. The indicated loading capacity for cyanide of about 10 percent was several times higher than achieved in previous work. Additionally,

complete removal of copper was obtained throughout the experiment indicating no losses of this component. The amounts of zinc adsorbed however were not established.

TABLE 19. CONTINUOUS ADSORPTION DATA FOR THE COPPER CYANIDE SYSTEM

Total Feed Solution Treated,[a] gal	Effluent Conditions		Apparent Percent Removal
	pH	ppm CN	
5	7.9	0.4	99.6
40	7.7	0.4	99.6
70	7.7	0.2	99.8
90	7.3	0.9	99.1
110	6.6	2.0	98.0
130	7.1	2.2	97.8
155	7.0	2.7	97.3
180	7.0	5.0	95.0
195	6.8	4.7	95.3
225	6.9	5.3	94.7
250	6.5	7.5	92.5
265	7.1	9.9	90.1
275	--	14.5	85.5

(a) Initial solution contained 75 ppm cyanide, 26 ppm cyanate, 66 ppm zinc, and 95 ppm copper.

To complete the evaluation of the copper cyanide system, preliminary experiments then were conducted on the regeneration of the loaded carbon. This work was done on both the entire volume of carbon used in the adsorption experiment and on small samples taken from the column.

Initial attempts to regenerate the carbon column were made with sulfuric acid and hydrochloric acid solutions. With 10 percent sulfuric acid regenerant, significant amounts of cyanide were removed from the column but the stripping required several hours. Approximately 34 grams of cyanide were removed which corresponded to about 50 percent of the adsorbed cyanide. Virtually none of the copper was removed.

In order to cover a wider range of regeneration conditions, samples of carbon were removed from the column after the sulfuric acid stripping and tested separately. The results of these small-scale tests are given in Table 20.

The results of these small-scale experiments indicated that several procedures could be used to effect efficient stripping. These included

TABLE 20. STRIPPING CONDITIONS AND RESULTS

Expt. No.	Weight Carbon g(a)	Stripping Solution	Temp.	Time, hr	Weight Loss, %(b)	%(c) Copper Removed	%(d) Cyanide Removed
1	2.0	Ammonium hydroxide 1:1	Room	5	9	55	55
2	2.0	Hydrochloric acid 1:2	Room	5	10	60	60
3	2.0	Hydrochloric acid 1:1	Room	16	18	95	95
4	10.0	10% NaCN, 5% NaOH	Room	16	18	95	95
5	0.5	25% H_2SO_4	Boiling	2	19	100	100
6	2.9	5% sodium hypochlorite to oxidize cyanide followed by 10% sulfuric acid to dissolve copper	Room	2	19	100	100

(a) Carbon used was removed from center portion of column and dried overnight at 110 C. By analysis it contained 11.8 percent copper and 3 percent CN.

(b) After stripping treatment, samples were filtered, washed with distilled water, dried, and weighed. Weight loss is a measure of the removal of cyanide, copper, and other adsorbed materials. Complete removal should result in a weight loss of approximately 20 percent, as judged by the weight loss of the sample used for cyanide analysis. Experiment 5 in the table shows the data obtained on the analytical sample.

(c) Based on copper analysis of combined stripping and washing solutions.

(d) Estimates based on assumption that cyanide removal parallels copper removal. Percentage of weight loss indicates that this assumption is reasonable.

treatment with hydrochloric acid, alkaline cyanide solution, sodium hypochlorite, sulfuric acid, etc. These experiments were made on small samples of loaded carbon that had been previously dried at 110 C. Work done at this time on carbon that had not been dried, however, was not as promising. For example, in an experiment in which 10 percent sulfuric acid was circulated through a bed of loaded carbon for 20 hours only about 50 percent of the cyanide and only a few percent of the copper was removed.

Because stripping with sulfuric acid in a system that would permit the recovery of copper and cyanide appeared to be more practical and possibly more economical for the smaller plater, emphasis was placed on investigating such a process.

A fresh lot of Pittsburgh OL carbon (500 grams) was charged into the adsorption column and loaded with copper cyanide by feeding 100 gallons of a solution containing 76 ppm of cyanide, 100 ppm of copper, and an estimated 25 to 30 ppm of cyanate (CNO) (arising from the oxidation of cyanide by cupric copper and/or air). The latter was used for agitation during solution preparation. Adsorption efficiency was excellent (99+ percent of the copper and 96-99 percent of the cyanide) during the adsorption cycle. The loaded carbon, by calculation, contained 36.1 grams of copper and 29.0 grams of cyanide. This carbon was then treated for 13 hours by recirculating a solution of 10 percent sulfuric acid through it at a flow rate of 300 ml per minute. During the recirculation, the pump reservoir of acid was constantly aerated. Exit gas from the reservoir was continuously passed through a caustic trap to collect cyanide vapors. At the end of the run, the acid solution was analyzed for copper and the caustic trap solution for cyanide. The results are shown in Table 21 (Run 1). They indicated that after 13 hours only 41 percent of the copper and 57 percent of the cyanide was removed.

Run 2 (Table 21) was made on the partially stripped carbon from Run 1. In this run, which was carried out for 18 additional hours, with 10 percent sulfuric acid under conditions of aeration, 100 percent of the remaining adsorbed copper was removed from the carbon. The conclusion that the additional 18-hour treatment alone was responsible for complete removal was not justified however. This was because the partially loaded carbon from Run 1 was used in an unsuccessful experiment to adsorb cyanide from an uncomplexed or free cyanide solution before attempting Run 2. It is conceivable that the treatment with free cyanide solution may have contributed to the complete removal of copper experienced in Run 2. Another possible contributing cause for the complete stripping achieved in Run 2 was that previous to the run, the carbon bed was drained and partially dried in the column.

Run 3 (Table 21) was made on the same 500-gram lot of carbon, which had been reloaded with copper and cyanide. The purpose of this run was to disclose the role played by the aeration procedure in the stripping of copper and cyanide. In this run, the agitation required to keep cyanide gas swept out of the circulating acid solution was supplied by bubbling nitrogen instead of air through the reservoir. The results indicated that

TABLE 21. LABORATORY STRIPPING OF COPPER AND CYANIDE FROM ACTIVATED CARBON

Stripping Conditions				Loaded Carbon			Percent Stripped	
Run No.	Time, hr	Stripping Medium	Aeration	Carbon, g	Copper, g	Cyanide, g	Copper	Cyanide
1	13	10% H_2SO_4	Yes	500	36.1	29.0	41	57[d]
2[a]	18	10% H_2SO_4	Yes	500	19.9	--	100	--
3[b]	16	10% H_2SO_4	No	500	36.3	29.0	15	35[d]
5[c]	58	10% H_2SO_4	Yes	500	42.7	--	100	100[e]

(a) This run was made on the carbon left from stripping Run No. 1; which still contained considerable copper and cyanide. However, before beginning this run, the carbon left from Run 1 had been subjected to treatment with 20 gallons of free cyanide solution containing 100 ppm of cyanide, in an experiment to determine whether copper-bearing carbon would adsorb free cyanide. This pretreatment may have contributed to the complete removal of copper.

(b) This run was made on the completely stripped carbon from Run 2, which had been reloaded by the adsorption of 100 gallons of solution containing 76 ppm of cyanide and 100 ppm of copper. No air was employed in this run and agitation to sweep cyanide out of the adsorbing acid was provided by bubbling a stream of nitrogen through the solution.

(c) This run was made on the partially stripped carbon from Run 3, to which additional copper had been added as copper sulfate. However, before this run, the column of copper-rich carbon had been unsuccessfully tested as a medium for adsorbing free cyanide. It is possible that this treatment with free cyanide may have contributed to the completeness of copper removal obtained.

(d) Based on analyses of absorbing caustic solution. Does not take into account CNO formation. Values shown, therefore, are somewhat low.

(e) Based on analyses of carbon after stripping, which indicated complete removal.

considerably less copper was stripped under these conditions than when air was used as in Run 1 (15 vs. 41 percent of the copper). It is believed that the oxidation of cuprous to cupric copper by air contributed significantly to the oxidation of cuprous cyanide and the consequent solubilization of copper.

In Run 5 (Table 21) complete stripping of copper and cyanide was again achieved. This run was made on the partially stripped carbon from Run 3 to which additional copper had been added. As in the case of Run 2, it was not justifiable to attribute the complete removal of copper and cyanide simply to the longer treatment with aerated acid. This was because prior to Run 5 the copper enriched partially loaded column had been used to determine its effectiveness as an adsorbent for free cyanide. Again, it is conceivable that the treatment with free cyanide solution may have contributed to copper removal. After Run 5, a sample of the carbon was removed from the column and analyzed for cyanide. The analyses (0.05 percent) indicated that cyanide removal also was virtually complete.

The results of Runs 2 and 5 showed that it was possible to strip completely both copper and cyanide from the carbon. What was not yet known was the relative importance of the conditions employed in these runs, i.e., time, aeration, pretreatment with dilute free cyanide solution, and partial drying of the bed. Also, in the stripping runs, a good material balance for copper was always obtained. The balances for cyanide, however, were poor with up to 50 percent of this component being unaccounted for. It is believed that during stripping, the missing portion of the cyanide was oxidized, either to cyanate, or carbonate, or was converted to ammonia; however, no analytical verification of these possible reactions was completed.

While the preceding studies were favorable to the continued development of a process based on the adsorption of a copper cyanide complex, uncertainty about various important aspects of such a process still existed. These were:

(1) The effect of multiple cycles of adsorption and stripping on the adsorptive capacity of the carbon.

(2) The requirements for effective stripping with sulfuric acid. The previous work did not rule out the possibility that for sulfuric acid stripping to be effective, it would have to be augmented by such operations as predrying of the carbon or pretreatment with alkaline cyanide solution before stripping.

(3) Cyanate formation. In the previous work about 20 percent of the original cyanide was converted to cyanate. It was believed that the major mechanism of cyanate formation was oxidation by the cupric copper sulfate used for complexing according to the equations:

$$3CuSO_4 + 6NaCN \rightarrow 2CuCN \cdot Cu(CN)_2 + (CN)_2 + 3Na_2SO_4$$

Copper sulfate; Sodium cyanide; Cupro·cupric cyanide; Cyanogen; Sodium sulfate

$$(CN)_2 + 2NaOH \rightarrow NaCN + NaCNO + H_2O \ .$$

Cyanogen; Sodium hydroxide; Sodium cyanide; Sodium cyanate

In the earlier runs, however, the solution was agitated by a stream of air during the entire period of solution preparation. It was considered possible that some cyanate may have been formed by the simple oxidation of cyanide according to the equation:

$$NaCN + 1/2O_2 \rightarrow NaCNO$$

Sodium cyanide; Sodium cyanate

During subsequent work, a series of multiple adsorption and regeneration cycles was made to resolve these uncertainties.

In order to expedite the completion of the multiple cycle series, it was decided to scale down the system. Instead of the 2-1/2-foot columns containing about 500 to 700 grams of carbon, which required about 100 gallons of solution per cycle, a smaller adsorption column containing only 125 grams of carbon was used. Conditions and results of the experiment are summarized in Table 22.

The Pittsburgh OL granular carbon showed excellent adsorption efficiency for the first 3 cycles adsorbing respectively 94, 100, and 100 percent of the copper and 91, 97, and 94 percent of the cyanide. The lower adsorption percentages obtained in Cycle 1 compared to those in Cycles 2 and 3 are believed due to the extremely high feed rate used in that cycle (corresponding to 30 to 40 gpm per 100 pounds of carbon. In Cycles 2 and 3, where lower feed rates were used (10 to 20 gallons per minute per 100 pounds of carbon) adsorption efficiency for both copper and cyanide improved. The short bed (12 inches) employed in these tests to save time contributed to some unmeasured extent in the failure to obtain 100 percent adsorption.

According to technical information supplied by the Pittsburgh Carbon Company which manufactures the carbon used in these experiments, a 10-foot-long bed of carbon is the minimum required for the accurate translation of laboratory data to practice. It is believed that had the recommended 10-foot-long columns been used, even higher adsorption efficiencies would have been obtained in Cycles 1 through 3.

The relatively poor adsorption obtained in Cycle 4 (80 percent for both copper and cyanide) is probably the result of a combination of factors:

TABLE 22. CONDITIONS AND RESULTS OF MULTIPLE CYCLE ADSORPTION-REGENERATION EXPERIMENTS

Cycle No.	Feed Solution Composition[a] Cu, ppm	CN, ppm	pH	Feed Rate, ml/min. (ℓ/min/lb C)	Volume Fed, liters (gal)	Wt C in Column, g	Effluent Composition[b] Cu, ppm	CN, ppm	pH	Adsorption, %[c] Cu	CN	Weight Adsorbed[c] Cu g	Cu lbs/100 lb of C	CN g	CN lbs/100 lb of C	Aeration of Acid	Intermediate Drying[d]	Stripping Hours	Wt[e] Stripped Cu	Wt[e] Stripped CN	Percent Cu	Stripped CN[f]
1	98	78	7.0	300-400 (29-38)	94 (25)	125[g]	5	7	2.3-7.0[h]	94	91	8.74	7.0	6.67	5.34	Yes	No	18	7.9	6.9	93	100+
2	98	78	7.0	100-200 (15-20)	94 (25)	129[g]	1	2	2.2-7.2[h]	100	97	9.21	7.7	7.12	5.95	Yes	No	37	6.8	6.4	83	93
3	98	78	7.0	80-100 (10-15)	94 (25)	115[g]	1	4.5	2.2-7.1[h]	100	94	9.21	8.0	6.83	5.96	Yes	No	28	7.1	5.9	77[a]	87
4	118	107	7.0	80-150 (10-20)	109 (27)	110[g]	24	21	2.2-8.5[h]	80	80	9.40	8.5	8.69	7.83	Yes	Yes	28	11.78	8.2	125	95
5	98	78	7.0	100-200 (15-20)	112 (30)	105[g]	15	16	2.3-7.7[h]	85	80	9.30	8.8	6.95	6.61	No stripping						

Footnotes on following page

Footnotes for Table 22.

(a) Standard feed solutions for Cycles 1 through 3 and 5 were made up by adding cupric sulfate to sodium cyanide solution, adjusting pH to 10 and agitating with air for 10 minutes to effect complexing; and then adjusting pH to 7.0 with dilute H_2SO_4. Compositions shown based on analysis of a single solution made by the standardized procedure. Feed solution for Cycle 4 was a composite of two different types of solutions. The first third of the run was made on a solution prepared by attempting to complex the free cyanide with metallic copper under conditions of aeration. When this appeared to be impractically slow in reducing free cyanide, cupric sulfate was added in small increments until free cyanide, by the specific CN ion meter showed 4 ppm. After 9 gallons of this material had been fed through, a break occurred in the solution lines during the night. The run was completed by feeding 18 gallons of the standard feed solution through the column. The composition shown for this feed solution is based on the analysis of a composite sample.

(b) For Cycles 1 through 3, Cu and CN compositions are based on average analyses of effluent samples. For Cycles 4 and 5, in which the effluents contained sufficient copper to interfere with the routine analytical procedure, compositions are based on analysis of the combined effluent.

(c) Based on feed and effluent analyses and on weight of carbon in column.

(d) Drying of the carbon in Cycle 4 done by passing a slow stream of air downward through the column for 12 hours. After drying, stripping with acid was begun.

(e) Based on analyses of acid stripping solution and caustic scrubbing solution.

(f) Weight stripped x 100 ÷ weight adsorbed.

(g) Reduction in weight of carbon from cycle to cycle due to removal of samples.

(h) pH at beginning of each cycle was as low as 2 to 3, but rose to the pH of the feed after a few gallons had been fed. In Cycle 4, the effluent pH exceeded the feed pH for an as yet unexplained reason. A similar though less pronounced situation occurred in Cycle 5.

(1) Feed solution composition. Two feed solutions were used in this run. The first third of the run was made with a solution in which the cyanide was complexed partially by metallic copper (cement copper and copper wool) and then, when this procedure was found to be too time consuming, by cupric sulfate. About 9 gallons of this solution had been passed through the column with an effluent containing 5 to 7 ppm of cyanide, and 3 to 5 ppm of copper, when a leak in the pump lines occurred and the remainder of the 25-gallon batch leaked to the sewer and escaped treatment. Following this a batch of the standardized solution as used in Cycles 1 through 3 was passed through the carbon. Almost from the outset, the effluent exhibited an anomalous behavior. The pH rose to 8.5 and significant amounts of both copper and cyanide began to appear in the effluent. These results point up the possibility that the attainment of proper complexing conditions--conditions that will give good adsorption--may be touchy and the desirability of specific studies to determine the workable limits within which solution compositions can be varied.

(2) Incomplete stripping of copper deposited on the carbon in previous cycles. Material balance data based on the data shown in Table 22 indicate that in the first three cycles 27.10 grams of copper were adsorbed by the carbon, whereas only 21.8 grams were removed by stripping, a difference of 5.3 grams. Analysis of the carbon after Cycle 3 stripping indicated that it still contained 3.1 grams of copper. The amount of copper stripped after Cycle 4 adsorption, 125 percent of that calculated to have been adsorbed in Cycle 4, reflects this continual buildup of copper on the carbon in the first three cycles. Previous work has shown that incomplete stripping leads to poor adsorption. It is quite probable that such incomplete stripping was a significant factor in the poor adsorption in Cycle 4.

(3) Decreased adsorptive efficiency of the carbon. It is possible that the adsorptive efficiency of the carbon deteriorates through some unexplained mechanism, with repeated adsorption and regeneration cycles. That serious deterioration in adsorptive powers occurs, however, is not considered likely, considering that the capacity of the carbon in Cycle 4 for copper and cyanide is great or greater than it was in Cycles 1 through 3.

The lower adsorption percentages obtained in Cycle 5 which was run with the standardized feed solution were somewhat disappointing, and might indicate a loss in the adsorption efficiency of the carbon. However, considering that 20 grams of the carbon had been removed by sampling and that the length of the bed was accordingly decreased by about 20 percent, it is believed that channeling of the solution contributed significantly to the amount of copper and cyanide in the effluent. As shown in Table 22, the loaded carbon from Cycle 4 contained 8.8 pounds of copper and 6.61 pounds of cyanide per 100 pounds of copper, which is comparable to the loadings obtained in the previous cycles. This fact provides some indication that the capacity of the carbon for copper cyanide was not seriously impaired.

Preliminary Evaluation of Treatment Costs

An attempt was made to assess the relative merits of the candidate cyanide treatment processes studied during the initial phase of the program. It was assumed that the cost of chemicals would be the most important indicator of the relative cost for these processes.

Ion Flotation. The costs involved in operating an ion flotation system were assumed to include primarily the flotation collectors and complexing chemicals which were added to effect removal. It was assumed that regeneration with recovery of chemicals was not feasible; the spent collector loaded with cyanide simply would be collected as a sludge and disposed of in some way, i.e., incineration, chemical oxidation, etc.

During the experiments, two approaches involving flotation of complex nickel and iron cyanides appeared to show good removals of cyanide. The efficiency of these approaches and the estimated reagent costs are shown in Table 23. On the basis of a typical plant having a waste flow of 15 gallons per minute containing 100 ppm of cyanide, it was estimated that the equipment costs for the ion flotation process would be about $4,000.

TABLE 23. EFFICIENCY AND COSTS OF ION FLOTATION OF COMPLEX CYANIDES

Reagent	Removal Attained,(a) %	Reagent Requirement,(a) lb/lb CN	Costs $/lb CN	Costs $/1000 gal
Iron Cyanide Solutions @ 10 ppm CN				
Ferrous Sulfate ($FeSO_4$) @ $0.01/lb		1.0	0.01	0.001
Amine Collector @ $0.33/lb	88	3.3	1.09	0.09
		Totals	1.10	0.09
Nickel Cyanide Solutions @ 10 ppm CN				
Nickel Sulfate ($NiSO_4$) @ $0.37/lb		1.5	0.56	0.04
Amine Collector @ $0.33/lb	93	13.3	4.39	0.35
		Totals	4.95	0.39

(a) Based on experimental data shown in Tables 7 and 8.

Activated Carbon Adsorption. In determining operating costs for the carbon process for cyanide removal, a number of important assumptions had to be made. Based on projected development and refinement of the process, it seemed reasonable to assume that the copper sulfate used for complexing could be almost entirely recovered and reused in the system. It also was assumed that the carbon could be regenerated indefinitely with no loss in adsorptive capacity; thus carbon replacement costs would be minimal. The major chemical consumed, therefore, would be sulfuric acid which was used for regeneration and pH adjustment in the complexing step.

On the basis of the laboratory experiments, about 5 pounds of sulfuric acid were used to adsorb and regenerate 1 pound of cyanide, indicating a cost of $0.10 per pound of cyanide removed (@ $0.02/lb H_2SO_4). Conservatively estimating a loss of 10 percent of the copper sulfate per regeneration, additional cost of about $0.07 per pound of cyanide would be incurred. Total chemical costs, therefore, could approach $0.17 per pound of cyanide treated. For the typical plant (15 gallons per minute at 100 ppm cyanide) equipment costs were estimated at $7,000.

Acidification-Volatilization. Preliminary estimates of the capital and operating costs for the acidification-volatilization process were made using the same estimating data and techniques employed above. Capital cost for a plant capable of treating 15 gallons per minute of waste was estimated at $8,500. The estimate is believed to be conservative.

The cost of reagents for this treatment were estimated based on laboratory data which indicated that a pH of 3 and temperature of 100 F would be used during treatment. The following tabulation shows how the reagent costs were calculated.

Reagent	Amount Required, lb/lb CN	Estimated Cost, $/lb CN
Sulfuric Acid @ $0.02/lb	18	0.36
Soda Ash[a] @ $0.025/lb	9	0.22
Sodium Hydroxide[b] @ $0.03/lb	3	0.09
	Total	0.67

(a) Assume half the weight of H_2SO_4 to bring the solution back to a higher pH before disposal.

(b) This is intended to provide enough caustic to adsorb HCN and CO_2 if it is not flared to the atmosphere.

Comparison of Processes. In addition to the above cost estimates for the experimental processes, the conventional method for cyanide treatment using sodium hypochlorite solution was evaluated. Using

the same basis mentioned previously, reagent and equipment costs were estimated at $1.35 per pound of cyanide and $6,500, respectively.

A comparison of these costs with those determined for the experimental techniques is shown in Table 24. This economic comparison indicates that the three experimental methods have somewhat lower costs than the conventional method with carbon adsorption showing the greatest advantage.

TABLE 24. COMPARISON OF COSTS FOR SELECTED TREATMENT METHODS

	Reagent Cost, $/lb CN	Capital Cost,(a) $	Operating Cost,(b) $/day
Ion Flotation	1.10	4,000	12.00
Carbon Adsorption	0.17	7,000	10.00
Acidification-Volatilization	0.67	8,500	12.50(c)
Conventional Method with NaOCl	1.35	6,500	15.00

(a) Based on waste flow rate of 15 gallons per minute and cyanide concentration of 100 ppm as CN.

(b) Based on 8-hour day, 250 days/year; waste flow rate of 15 gallons per minute, and 100 ppm CN. Includes cost of reagents; estimates of the cost of labor, power, and fuel; maintenance at 5 percent per year; and depreciation at 13 percent per year.

(c) Includes in addition to the items in (b), a credit for recovery of sodium cyanide at $0.20/lb.

Phase 2: Pilot-Scale Investigation

Equipment and Procedures

The second phase of experimental work on the activated carbon process was conducted in pilot-plant equipment employing two 1-foot-diameter columns each 6 feet tall and packed with activated carbon. The system was installed at a plating plant in Columbus, Ohio, and operated on actual waste zinc cyanide rinse waters produced at this plant. The plant had available two zinc cyanide plating lines from which rinse water could be obtained--one an automatic barrel line and the other an automatic rack conveyor. During operation of the lines, the entire waste rinse water flow was mixed in a floor drain and discharged to a common sump leading to the sewer. Combined flow was 25 to 50 gpm with cyanide concentrations up to 50 ppm.

The system was operated initially on combined rinse waters from both lines. For the majority of later runs, only concentrated cyanide rinse water from the barrel line was used. Figure 13 shows photographs of the barrel plating line, the pilot-plant waste treatment system, and the point of collection of the concentrated cyanide rinse waters.

The equipment shown in Figure 13c consisted basically of two 1000-gallon rubber-lined tanks, an adsorption module containing two carbon columns, and associated pumps, piping, and instruments to operate the system. Each column was filled with 100 pounds of Pittsburgh Type OL activated carbon. The unit includes piping, closed top polyethylene tanks, and valves to permit recirculation of the regenerating solutions.

The procedures used in operating the pilot-plant system were developed and modified as the study progressed and several modifications were employed.

In preliminary adsorption runs, mixed rinse waters from both plating lines were used as feed to the system. These rinse waters contained about 50 ppm of cyanide and smaller quantities of zinc, iron, and hexavalent chromium. The objective of these preliminary trials was to evaluate adsorption efficiency on the waste solutions as they were actually produced by the plant and then compare the results with an improved procedure which involved addition of copper to the rinse water and subsequent adsorption of complex copper cyanides. As discussed below, these runs showed unexpected results, so that it was decided to use only concentrated cyanide rinse waters produced by the barrel plating line. These rinse waters were collected as shown in Figure 13b from a primary rinse tank immediately following the plating tank in the normal operating sequence of the line. The rinse waters contained 300 to 400 ppm of cyanide.

Following a preliminary operation with the concentrated rinses, the following general procedure was used for subsequent detailed adsorption runs:

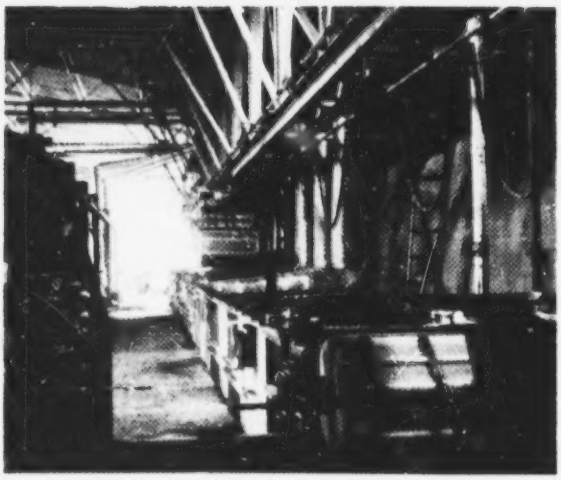

FIGURE 13a. AUTOMATIC BARREL PLATING LINE AT SUPERIOR PLATING COMPANY

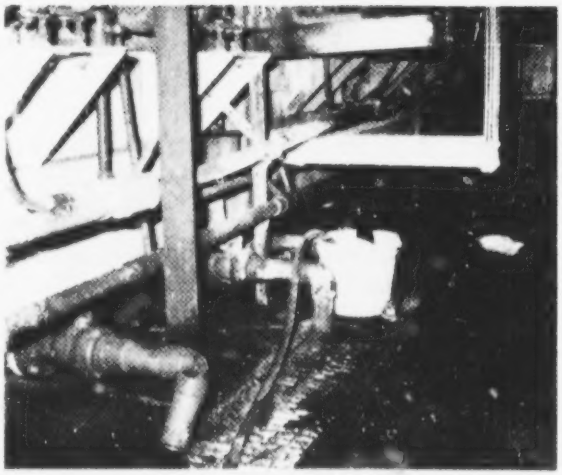

FIGURE 13b. COLLECTION POINT FOR CYANIDE RINSE WATER

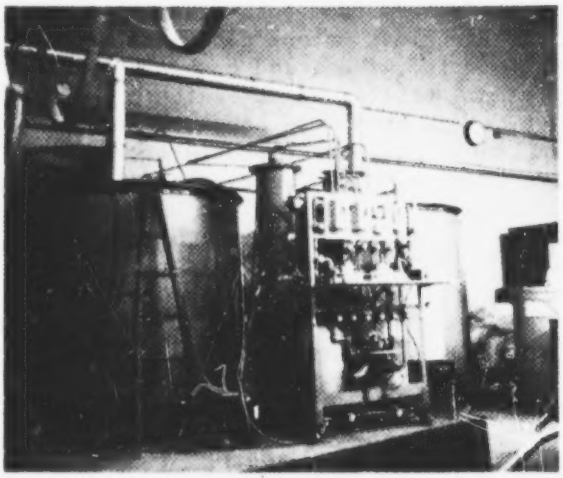

FIGURE 13c. PILOT-PLANT CARBON ADSORPTION SYSTEM

(1) Concentrated rinse water was pumped from the plating line at 2-3 gpm and collected in one or both of the 1000-gallon holding tanks.

(2) The solution was agitated by high pressure air and analyzed for cyanide content by the standard analytical procedure.

(3) Copper sulfate solution (60 gpl Cu) was added and the solution agitated for 10 minutes to effect formation of the complex copper cyanide. A pH of 10 was maintained during this time by addition of sulfuric acid, if necessary. For most runs, a copper to cyanide ratio of 0.75 by weight was selected.

(4) After complexing, the solution was adjusted to a pH of 6-7 by adding sulfuric acid; the precipitate which was formed was allowed to settle for a period of at least one hour. The supernatant clear liquid was pumped to the adsorption column at a rate of 2-3 gpm.

(5) Effluent from the adsorption column was discharged to the sewer.

The above procedure was employed in batchwise manner to effect loading of the carbon column until a breakthrough was achieved. The breakthrough point was selected as the time at which copper first appeared in effluent samples from the system. This normally was measured by qualitatively testing the effluent with dilute acid and observing the presence of colloidal $Cu(CN)_2$. Throughout the entire adsorption cycle, samples of both the feed and effluent solutions were obtained periodically for chemical analysis.

Regeneration runs on the loaded carbon bed normally were carried out after each adsorption cycle. The procedures used for regeneration also were subject to modification during the pilot-plant campaign. Based on previous work, the required methods consisted of recirculating a dilute aerated acid solution through the carbon bed for a period of about 24 hours. This effectively stripped both copper and cyanide from the carbon, leaving copper dissolved in the acid solution as cupric sulfate and producing hydrogen cyanide vapors which were then swept out of the acid solution. The use of air injected into the carbon column along with the sulfuric acid was found to be essential to oxidize cuprous to cupric copper, thereby breaking the copper cyanide complex to liberate cyanide. (In pilot-plant runs, air introduced into the acid solution did not accomplish this end.)

It was necessary to supplement the acid treatment of the carbon with a final caustic wash and to readjust the column effluent to pH 7. It is believed that this final treatment eliminated any residual adsorbed acid and effected greater adsorption efficiencies in the subsequent adsorption step.

Preliminary Results

Initial pilot-scale experiments on cyanide adsorption were begun with mixed rinse waters from both plating lines being used as feed to the system. These rinse waters contained about 50 ppm of cyanide and smaller quantities of zinc, iron, and hexavalent chromium. The objective was to evaluate adsorption efficiency on waste solutions as they were presently produced at the plant, without addition of copper to effect complexing of the cyanide. Pertinent operating data for these runs are shown in Table 25.

It was found that an unexpectedly high adsorption of cyanide was obtained from these mixed rinses. In Run 1, for example, a total of about 3100 gallons of rinse water was fed to the system before cyanide was observed in the effluent samples. The apparent adsorption capacity of the column during this run was 1.2 pounds of cyanide per 100 pounds of carbon, a value which was several times greater than that achieved in laboratory studies using synthetic zinc cyanide rinse waters.

It was suspected that the unusually high adsorption capacity in Run 1 was caused by the presence of iron in the mixed rinse waters used as feed. During a preliminary regeneration with sulfuric acid, a blue-colored solution was formed which indicated the presence of complex iron cyanides. Chemical analysis of this regenerating solution indicated 1570 ppm total iron, an amount equivalent to 16 ppm total iron in the feed solution used during the adsorption.

Although the presence of iron in the rinse waters seemed beneficial in the form of a complexing agent, at least some of the iron was not complexed and formed a ferric hydroxide precipitate which tended to clog the carbon column and thus prevent operation at the desired flow rates. In Run 2, a high level of adsorption was again achieved with mixed rinse waters at a pH of 9.5; however, the run was terminated when flow rates decreased to 1.0 gpm at a pressure drop of 8 psig through the column. Normal flow rates (2.0 gpm) were restored only by flushing the column with a dilute sulfuric acid solution.

Subsequent experiments then were conducted employing copper sulfate to complex cyanide in the rinse water solutions. Due to uncertainties regarding the mixed rinse waters and the inability to control this stream, it was decided to employ a separate concentrated cyanide rinse water produced only from one location in the plant. This rinse stream was collected from the overflow of a 2-stage countercurrent rinse tank immediately following the zinc cyanide barrel plating tank (see Figure 13b).

The adsorption data on initial pilot-plant runs with complexed copper cyanide feed solution are shown in Table 26. These runs were conducted initially by diluting the strong cyanide rinse stream from the plating line to about 100 ppm cyanide using tap water. Copper sulfate then was added using the procedures described previously.

TABLE 25. PRELIMINARY PILOT-PLANT ADSORPTION DATA ON MIXED CYANIDE RINSE WATERS

	Feed Data				Effluent Data			Cyanide Adsorbed		Indicated Loading Capacity,
	Gallons	pH	ppm CN	ppm Cu	pH	Typical ppm CN	Final ppm CN	lb	%	lb. CN/100 lb carbon
Run 1	3130	6.4-7.7	42-49	0[(a)]	6.8-9.5	<1.0	17	1.2	>98	1.2
Run 2	280	9.5	65	0[(a)]	8.1-9.5	<1.0	<1.0	0.1	>98	--

(a) No copper was added in these initial runs to evaluate adsorptive capacity on waste waters "as produced" at the plating plant.

TABLE 26. PRELIMINARY PILOT-PLANT ADSORPTION DATA ON THE COPPER CYANIDE SYSTEM

Run No.[a]	Feed Data					Effluent Data			Weight Adsorbed			Indicated Loading Capacity, lb, CN/100 lb carbon
	Gallons	Hours	pH	CN, ppm	Cu, ppm	pH	Typical CN, ppm	Final CN, ppm	lb CN	lb Cu	% Cu	
3a	807	5	6.7	68	100	8.1	<1.0	<1.0	0.46	0.67	>98	--
3b	450	6	7.6	91	100	8.9	<1.0	<1.0	0.34	0.38	>98	--
							Run 3 Totals		0.80	1.05	>98	0.8
4a	1630	26	7.1	96	113	7.0-8.9	<1.0	<1.0	1.31	1.54	>99	--
4b	1317	12	--	44	113	8.9	<1.0	<1.0	0.48	1.24	>98	--
4c	1623	16	7.4	98	113	8.1	<1.0	<1.0	1.33	1.53	>99	--
4d	1370	16	11.2	336	189	10.2	>347	347	Assumed to be zero			--
4e	703	9	6.5-11.2	455	189	9.2-11.1	400	153	Assumed to be zero			--
							Run 4 Totals[b]		3 12	4.31	>98	3.1

(a) These runs were performed on a fresh carbon bed of 100 lb Pittsburgh OL Carbon.
(b) Based only on first part of run in which high adsorption was achieved.

In adsorption Run No. 3, effluents from the carbon column containing less than 1.0 ppm of cyanide were consistently produced from feed solutions containing 68 to 91 ppm cyanide and about 100 ppm of copper. General operation in this run, however, was unsatisfactory due to an increase in pressure drop through the carbon column caused by solids which had precipitated from the feed solution. Run No. 3 was terminated after feeding about 1250 gallons. The column was washed for 3 hours with 10 percent sulfuric acid. Run No. 4 was started immediately following the acid wash, which had effectively eliminated the high pressure drop through the column.

In the first part of Run No. 4, adsorption was again carried out on dilute solutions. Approximately 3.12 pounds of copper were adsorbed during this period with adsorption efficiencies greater than 98 percent. In the later stages of the run, an attempt was made to feed strong cyanide solutions as collected from the plating line without dilution. Operating conditions in this latter part of the run were not optimum and very poor adsorption was observed. The inability to closely control the feed composition (pH and ratio of copper to cyanide) was believed responsible for the poor operation. This run was terminated when high levels of adsorption could not be reestablished.

Results obtained in preliminary regeneration studies on Runs 1 through 4 are summarized in Table 27. As previously indicated, attempts to regenerate the carbon after Run 1, in which mixed rinse waters were used, confirmed the observation that significant adsorption of cyanide occurred during this run, presumably as the iron complex. As can be seen, a total of 0.65 pound of cyanide and 0.33 pound of iron was stripped from the carbon during 48 hours of regeneration. Also of significance was the fact that measurable quantities of chromium also had been adsorbed during the operation.

Three difficulties were encountered: (1) the stripping of cyanide from the column for Run 1 was slow, requiring 48 hours to remove about 50 percent of the adsorbed cyanide, (2) the stripping of cyanide was incomplete, and (3) cyanide was not effectively and rapidly removed from the sulfuric acid regenerating solution by air sparging. A similar behavior also was observed in Regeneration Run 2. These preliminary runs point out that iron cyanide complexes very probably cannot be effectively stripped by a simple treatment with sulfuric acid, and that additional steps would be needed to achieve a successful approach.

The preliminary data on regeneration of copper cyanide complexes (Runs 3 and 4 shown in Table 27) also indicate the very slow stripping of cyanide and copper from the carbon that was observed in the pilot-plant system. Results from Run No. 4, for example, indicate that only about 40 percent of the cyanide was removed in 32 hours. It was found, however, that copper removal was dependent primarily on the method of introducing air into the system. The use of air was found to be a critical factor in laboratory studies and was believed to oxidize cuprous to cupric copper, thereby breaking the copper cyanide complex and liberating the cyanide. Air introduced into the acid solution in the pilot plant was not effectively

TABLE 27. PILOT-PLANT DATA ON STRIPPING OF CYANIDE COMPLEXES

Run No.	Column[a] Number	Regenerating Solution: Volume, gal	Regenerating Solution: H_2SO_4, lb	Regenerating Solution: Type of Aeration	Hours	Intermediate Drying of Carbon	Weight Stripped, lb: CN	Cu	Fe	Cr	Percent Stripped: CN	Cu
1	1	25	20	Acid sparging	48	No	0.65	0	0.33	0.05	54	--
2	1	25	20	Acid sparging	8	No		Negligible			--	--
3	2	25	16	Acid sparging	3	No	0.03	trace	0.14	--	4	0
4a	2	25	20	Acid sparging	16	No	0.68	0.02	0.07	--	--	--
4b	2	25	3	Acid sparging	16	No	0.35	0.04	0.02	--	--	--
4c	2	25	6	Column Injection	40	Yes	0.19	0.84	--	--	--	--
4d	2	25	4	Column Injection	40	No	0.08	3.49	--	--	--	--
					Run 4 Totals		1.30	4.39	0.09		42	100

(a) Both columns charged with 100 lb Pittsburgh OL Carbon.

used as shown by the results for Runs 4a and 4b in Table 25. Much better results were obtained in Run 4c when the column was predried with air and when air was injected directly into the column along with the acid regenerant.

Results of Multiple Cycle Adsorption and Regeneration Runs

Following the preliminary operation, a series of multiple cycle adsorption and regeneration runs were conducted on a single carbon bed using concentrated cyanide rinse waters containing from about 200 ppm to over 350 ppm cyanide. The data obtained during this multiple cycle operation are presented in Tables 28 and 29.

For adsorption cycles, the standardized procedure described previously was used for all runs. One additional step was included in an attempt to eliminate the formation of precipitates from the feed to the column. This consisted of allowing the solution to settle in the holding tanks for a period of at least one hour after adjusting the pH to a value of 7. This settling procedure effectively reduced the amounts of the zinc hydroxide and iron compounds which previously had caused clogging of the carbon column. The settled sludges produced in the feed tanks were analyzed to determine what percentage of the contaminants were removed by settling.

As can be seen from the data in Table 28, adsorption efficiencies for cyanide and copper were good through 5 cycles of operation. Copper removal remained virtually complete (greater than 99 percent) in each cycle up to the point of breakthrough. The adsorption of cyanide decreased in Cycles 2 and 3 to a low of about 80 percent and then improved to about 98 percent in Cycles 4 and 5. This poorer performance in Cycles 2 and 3 was subsequently traced to an improvement discovered in regeneration for preceding cycles. Following Run 3, the regeneration procedure was modified to include a final treatment of the carbon with caustic to readjust the column pH to a value of 7 just prior to the succeeding adsorption. This final caustic treatment improved adsorption efficiencies for Cycles 4 and 5.

Discussion of Pilot-Plant Runs

The results of the pilot-plant study demonstrated that real zinc cyanide rinse waters can be effectively treated by a carbon adsorption process and that the method will produce effluents which will meet current regulations governing discharges of cyanide to municipal sewers. One of the major goals of the study was to demonstrate that the carbon does not lose its adsorptive capacity after repeated adsorption-regeneration cycles. During the study, the adsorptive capacity of the carbon remained high after 5 cycles of adsorption and regeneration, indicating that the column

TABLE 28. RESULTS OF MULTIPLE CYCLE ADSORPTION AND REGENERATION RUNS ON CONCENTRATED ZINC CYANIDE WATERS

		Typical Concentrations, ppm			Weight, pounds		Efficiency, percent	
	Component	In Feed	Effluent Average	Effluent at Breakthrough	Adsorbed	Stripped	Adsorption	Regeneration
Cycle 1, 2460 gal treated	Cyanide, CN	220-340	1	61	5.88	1.67	>99	28
	Copper, Cu	240-317	<1	30	5.47	5.06	>99	92
	Iron, Fe	6-17	2	12	0.33	0.03		10
Cycle 2, 1770 gal treated	Cyanide, CN	239-364	30	94	(4.93)	1.05	≈90	21
	Copper, Cu	145-252	<1	43	4.10	3.09	>99	75
	Iron, Fe	0.1-16.7	2	0.2	--	0.01	--	--
Cycle 3, 1800 gal treated	Cyanide, CN	203-270	50	60	3.73	0.97	≈80	26
	Copper, Cu	164-214	<1	32	3.06	2.87	>99	94
	Iron, Fe	1.3-8.5	--	0.2	--	0.18	--	--
Cycle 4, 3540 gal treated	Cyanide, CN	234-436	2	31	7.36	0.89	98-99	12
	Copper, Cu	170-365	<1	5.8	6.72	5.59	>99	83
	Iron, Fe	0.3-33	0.3	--	0.26	0.13	--	50
Cycle 5, 4100 gal treated	Cyanide, CN	333-468	2-3	--	10.15	--	98-99	--
	Copper, Cu	224-330	<1	--	9.57	--	>99	--
	Iron, Fe	0.3-21	0.3	--	0.33	--	--	--

TABLE 29. CONDITIONS AND RESULTS OF REGENERATION FOR MULTIPLE CYCLE EXPERIMENT

Cycle No	Regenerating Solution				Wash Water, gallons	Amount Stripped, lb		
	Gallons	lb H_2SO_4	lb NaOH	Hours		CN	Cu	Fe
1a	25	12	0	9	--	1.43	0	0.005
1b	25	16	0	104	20	0.24	5.06	0.029
				Cycle 1 Totals		1.67	5.06	0.034
2	25	20	0	104	35	1.05	3.09	0.011
3a	25	20	0	120	35	0.52	2.79	0.026
3b	30	0	9(a)	2	--	0.45	0.08	0.150
				Cycle 3 Totals		0.97	2.87	0.176
4a	25	26	0	≈200	35	0.52(b)	5.42	0.031
4b	30	0	10(a)	1	15	0.37	0.17	0.102
				Cycle 4 Totals		0.89	5.59	0.133

(a) In these runs, a final caustic wash was given to the carbon bed after draining the acid regenerant. Column pH finally was adjusted to 7.

(b) Samples of the loaded carbon near the top of the bed was removed after 24 hours had elapsed in this regeneration cycle and analysed for total cyanide. The analyses showed 3.5 lb CN/100 lb carbon.

performance was maintained provided the acid regeneration was followed by a caustic wash prior to the next sorption step. Not enough cycles were conducted during the campaign to fully evaluate the life of the carbon bed, although these results indicate little or no diminution of the affinity of the carbon for the copper cyanide complex.

Another aspect of the process which was not fully investigated involves stripping of the copper and cyanide from the carbon during regeneration. Complete stripping of copper generally occurred during all runs with a minimum of 90 percent recovery. However, the stripping procedure required successively longer periods as the number of cycles increased, an as yet unexplained effect. In addition to longer stripping periods, the accountability of cyanide stripped from the carbon became progressively poorer as the number of cycles increased. This effect was not as noticeable in previous laboratory studies.

SECTION VI

ECONOMIC EVALUATION OF THE CARBON SORPTION PROCESS

On the basis of pilot-scale studies conducted in Phase 2, capital and operating costs for the carbon adsorption process were reevaluated. The results of Phase 2 indicated the desirability of including several modifications and/or alternatives which were not considered originally.

Two hypothetical treatment systems were considered: (1) a manually operated system similar to the unit used in pilot-scale work, and (2) a semicontinuous process designed to require a minimum of attention by the user. Both systems were based on a wastewater flow of 10 gallons per minute containing 300 ppm of cyanide. It is believed that both systems can be applied successfully to the treatment of cyanide rinse waters which contain cadmium or copper as well as to the zinc rinse waters used in the experimental work. Small amounts of other heavy metals such as iron or chromium also may be present.

Flowsheets for these proposed carbon systems are illustrated in Figures 14 and 15. During operation, the rinse water first would be introduced into the tank where the pH would be adjusted to a value of 10. Enough copper sulfate would be added to completely complex any free cyanide in the solution. After mixing for 10 to 20 minutes, the solution would be neutralized to pH 7 with sulfuric acid. In the manual system (Figure 14), these steps all would be conducted in the feed collection tank by a plating plant operator. In the continuous system (Figure 15), it is believed that appropriate controls and instruments could be used to conduct the steps automatically and continuously.

Following these initial steps, the solution would be allowed to settle to minimize the amount of suspended solids sent to the carbon columns. If the solids are settled, a sludge would be produced and allowed to accumulate in the feed tanks for removal at weekly intervals. The precise disposition of this sludge was beyond the scope of this work. It is believed that the sludge could be dewatered and disposed of without the need for excessive additional treatment.

The clear effluent after settling then is passed through carbon adsorption columns which remove all copper and at least 99 percent of the cyanide. The treated effluent is discharged to the sewer.

Periodically, the carbon beds must undergo regeneration to remove the load of adsorbed copper cyanides. It is believed that with some further development work, the adsorption and regeneration cycle could be accomplished with a two-column system on weekly intervals. The regeneration step produces a waste gas stream, an acidic solution of copper sulfate, and a caustic solution containing small amounts of ferrocyanides if iron

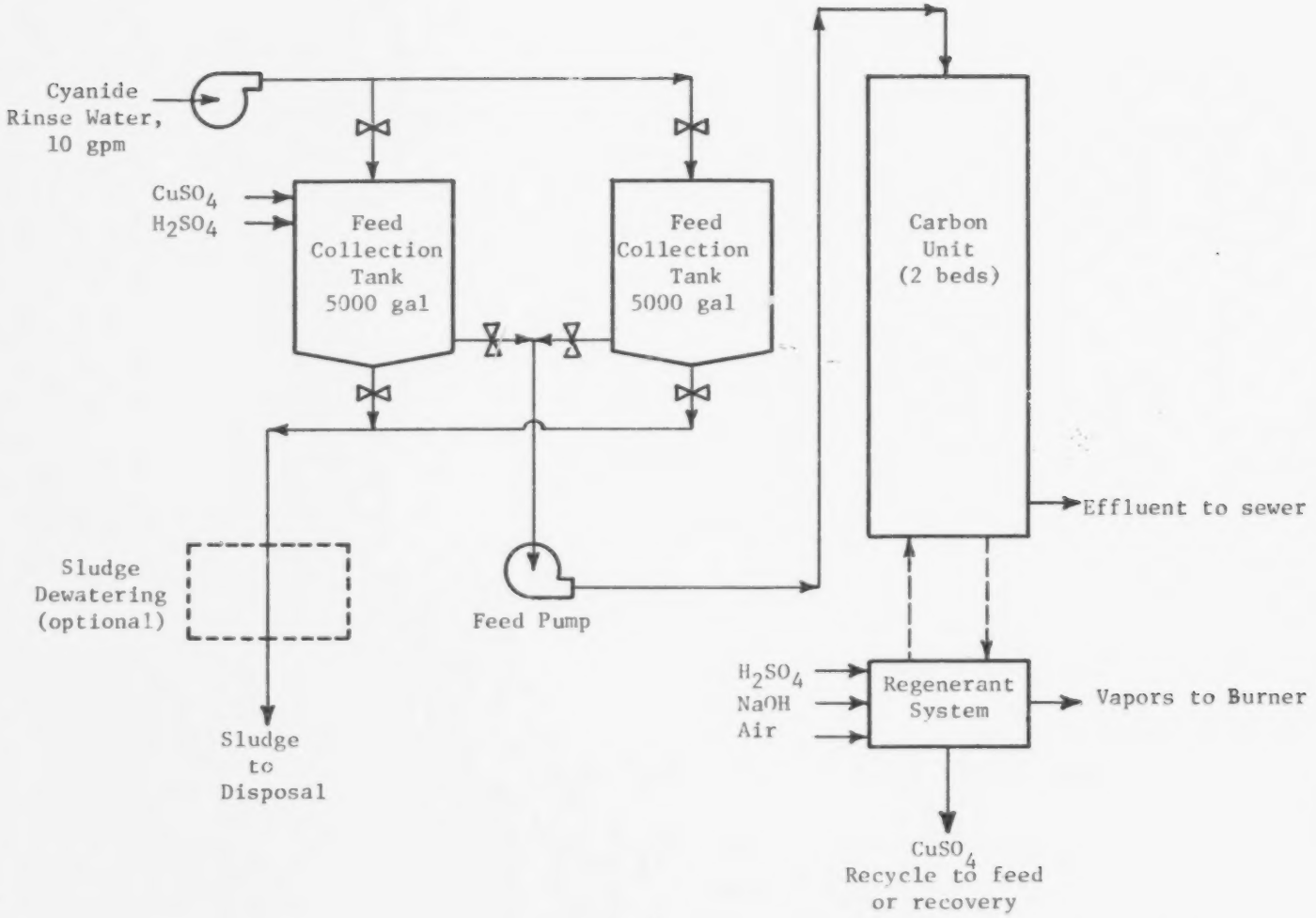

FIGURE 14. SYSTEM I: FLOW DIACRAM OF BATCH OR MANUALLY OPERATED CARBON PROCESS

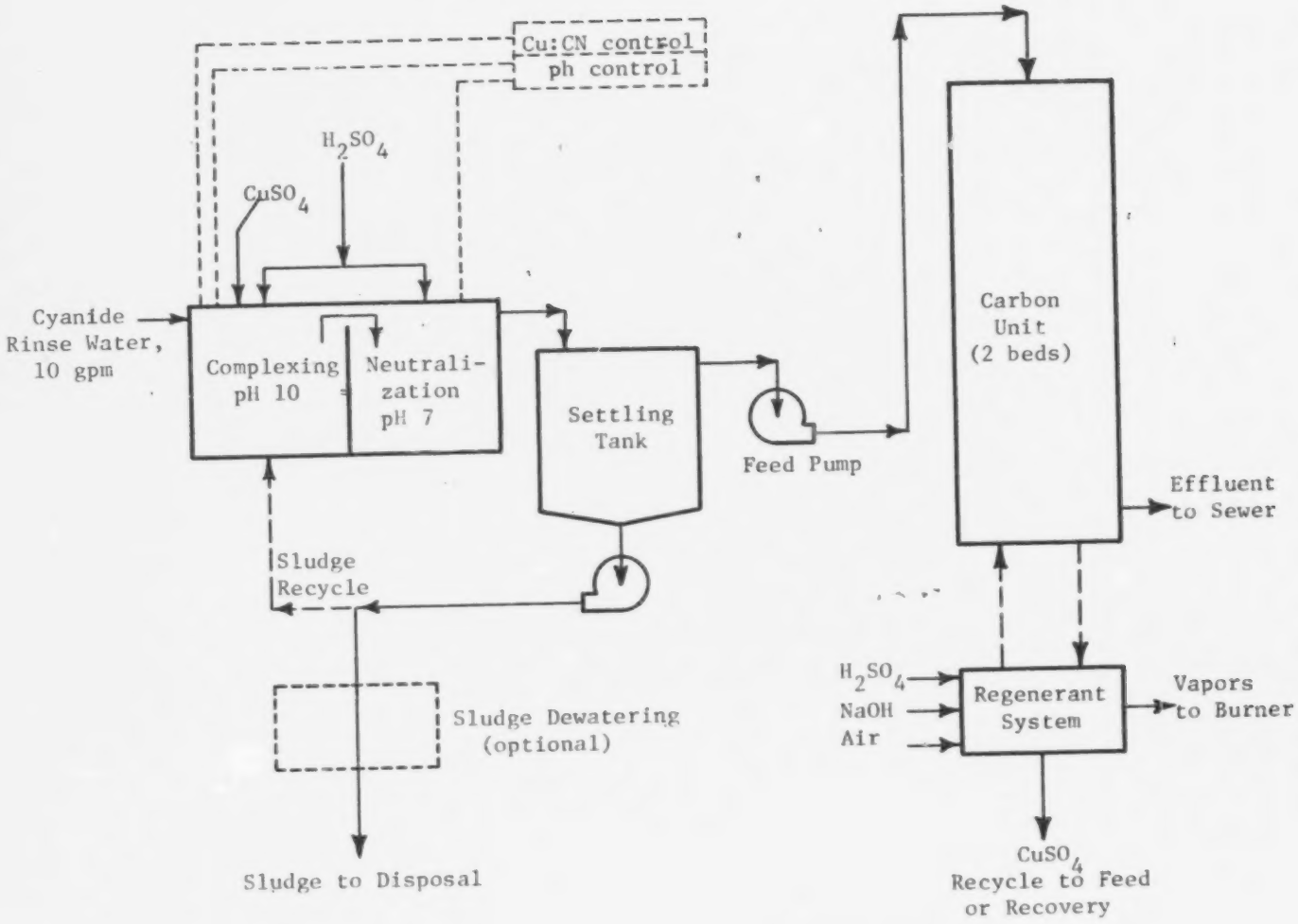

FIGURE 15. SYSTEM II: FLOW DIAGRAM OF CONTINUOUS CARBON PROCESS

is present in the feed solutions. The waste gases, which were found in pilot-scale work to contain about 1 percent of hydrogen cyanide (HCN) and varying amounts of carbon dioxide, would be passed through a burner before being exhausted to the atmosphere. Spent caustic would be either neutralized or fed back to the feed solution tanks. The copper sulfate solution would be used as recycle for subsequent complexing of the feed stream. Alternately, it is believed that a portion of the copper sulfate could be sent to a recovery step if sufficient copper was originally present in the cyanide rinse waters. This recovery was assumed to provide a credit toward the cost of operating the process.

Equipment and operating costs were estimated for each of the two waste treatment systems described above. As shown in Tables 30 and 31, the estimated plant equipment costs are about $12,000 for the manual system and about $16,000 for the continuous system. The estimate for the continuous operation is more speculative because the required procedures, instrumentation, and controls have not been developed experimentally during this program.

In summarizing operating costs, the important aspects are that the cost of chemicals totals about $0.30 per pound of cyanide removed for each of these processes. Estimated total operating costs (including labor, power, fuel, supplies, maintenance, and amortization) range from $10 to $14 per day. These estimates were based on the assumption that no copper would be present in the feed rinse and that the amount of copper used for complexing would be completely recovered during regeneration and recycled within the process. The value of the copper sulfate used in the process is considerable and could represent a credit to the operation if sufficient copper were originally present in the feed rinse waters. The net operating costs shown in this table indicate the effect of applying a credit for copper sulfate recovery. It is significant to note that net operating costs probably could be reduced nearly to zero in the case of 16-hour-per-day operation for System II.

TABLE 30. PURCHASED EQUIPMENT COSTS FOR EXAMPLE CARBON SYSTEMS

		Cost, $
System I: Manual Operation		
Essential Equipment:		
(1) Carbon unit; two columns, regenerant tanks, feed pump, piping, and valves		7,000
(2) Feed tanks; two 5000 gallon		3,000
(3) Pump; 10 gpm		250
(4) pH meter		400
	Subtotal	10,650
Optional Sludge Removal:		
(1) Filter		1,000
(2) Pump		250
	Total	11,900
System II: Continuous Operation		
Essential Equipment:		
(1) Carbon unit; two columns, regenerant tanks, feed pump, piping, and valves		7,000
(2) Tanks; two 250 gallon, agitated, and one 2000 gallon		1,500
(3) Reagent feeders; two each		750
(4) Pump; 10 gpm		250
	Subtotal	9,500
Optional Sludge Removal:		
(1) Filter		1,000
(2) Pump		250
Instrumentation and Controls:		5,000
	Total	15,750

TABLE 31. ESSENTIAL OPERATING COSTS FOR EXAMPLE CARBON SYSTEMS

	System I Cost, $/day	System II Cost, $/day	
	8-hr day	8-hr day	16-hr day
Chemicals Consumed:			
(1) H_2SO_4 (complexing) 3.3 lb/lb CN @ 3c/lb	1.20	1.20	2.40
(2) H_2SO_4 (regeneration) 4 lb/lb CN @ 3c/lb	1.44	1.44	2.88
(3) NaOH (regeneration) 1 lb/lb CN @ 6.5c/lb	0.78	0.78	1.56
Subtotal	3.42	3.42	6.84
Other Operating Costs:			
(1) Labor @ $3.50/man-hr	3.50	1.75	1.75
(2) Power @ $0.010/kwhr	0.20	0.40	0.80
(3) Fuel @ $0.25/$10^6$ Btu	0.30	0.30	0.60
(4) Supplies and maintenance @ 0.003% of plant cost	0.36	0.47	0.47
(5) Amortization @ 0.0224% of plant cost	2.69	3.53	3.53
Subtotal	7.05	6.45	7.15
Total operating cost: $/day	10.47	9.87	13.99
Cyanide removal, lb CN/day	12	12	24
Copper sulfate recovered: lb $CuSO_4$/day[a]	0-23	0-23	0-46
Possible credits @ $0.345/lb $CuSO_4$: $/day	0-7.93	0-7.93	0-15.86
Net Operating Cost: $/lb CN	0.21-0.87	0.16-0.82	0-0.58

(a) It was assumed that copper was originally present in the rinse water and might range from 0 ppm up to 225 ppm copper.

SECTION VII

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APPENDIX

CONVENTIONAL METHODS FOR TREATMENT OF CYANIDE WASTEWATERS

SECTION VIII

APPENDIX

CONVENTIONAL METHODS FOR TREATMENT OF CYANIDE WASTEWATERS

Because of the toxicity of most cyanide compounds, the elimination of cyanides from rinse waters produced in metal-finishing operations has been standard practice for many years in the larger installations. The techniques which have been developed can be categorized as follows:

(1) Complete destruction of the cyanide ion with the formation of nitrogen,

(2) Conversion of the cyanide ion to the considerably less toxic cyanate ion, and

(3) Conversion of the cyanide ion to some other less toxic form such as the ferrocyanide ion.

Complete Destruction of Cyanide

Cyanide in rinse waters can be completely destroyed by treatment with chlorine gas in an alkaline solution at room temperature. The cyanide radical, CN, is disrupted with the carbon fragment being converted to carbonate and the nitrogen to nitrogen gas. The reaction involved is:

$2NaCN$	+	$5Cl_2$	+	$12NaOH$	→	N_2	+	$2Na_2CO_3$	+	$10NaCl$	+	$6H_2O$.
Sodium cyanide		Chlorine		Sodium hydroxide		Nitrogen		Sodium carbonate		Sodium chloride		Water

In the chlorination step, which is conducted under highly alkaline conditions, most of the heavy metals that accompany cyanide in the rinse waters precipitate as hydroxides, or possibly as ferro or ferricyanides. These latter compounds respond slowly to the chlorine treatment and, if permitted to settle out, probably receive little or no treatment. For this reason, vigorous agitation is required in the process.

The process can be carried out on a batch or continuous basis. If done batchwise, it requires the installation of rather large tanks for storing the rinse waters before treatment and usually requires the installation of duplicate tankage--each capable of undergoing treatment while the other is filling. Recommended tank sizes vary, ranging in capacities corresponding to from 2 to 24 hours of operation. If done continuously on a flow-through basis, this process must be instrumented to control the reagent additions and the quality of the effluent.

Sludge formation nearly always accompanies the chlorination process. The sludge is composed of the precipitated metal hydroxides and, if the lime is used to provide the alkalinity, it also contains calcium carbonate and possibly calcium sulfate. In some cases the volume of sludge produced may be too great for disposal to sewers and provisions for dewatering the sludge must be incorporated in the plant.

The suitability of this process for the smaller plater has been questioned by some authorities, primarily because of the potential hazards, the difficulty in handling, metering, and distributing the chlorine gas, and the need for maintaining the proper conditions of alkalinity in the solution to prevent formation and evolution of poisonous cyanogen chloride. Nevertheless, this process is widely used in the large metal-finishing plants and is described frequently in the literature.

Cyanide also may be completely destroyed by hypochlorites such as sodium hypochlorite (NaOCl), calcium hypochlorite [$Ca(OCl)_2$], or bleaching powder ($CaOCl_2$). An example of the probable reaction--analogous to the reactions with chlorine gas in an alkaline medium--is shown in the following equation:

$$2NaCN + 5NaOCl + H_2O \rightarrow N_2 + 2NaHCO_3 + 5NaCl\ .$$

Sodium cyanide	Sodium hypochlorite	Water	Nitrogen	Sodium bicarbonate	Sodium chloride

The process is relatively simple and consists essentially of adding the hypochlorite, either as a solution or as a solid to the rinse water. No additional alkalinizing agent, such as sodium hydroxide or hydrated lime, is required, as in the chlorine gas process.

Agitation also is required with hypochlorites. The process with hypochlorites may be conducted batchwise or continuously. This process probably is best suited to the needs of the smaller plater who is faced with the necessity for complete destruction of cyanide.

Advantages of hypochlorite processes over the chlorination process are:

(1) If sodium hypochlorite or calcium hypochlorite are used, the theoretical chlorine consumption is only half as great as that if chlorine gas is used. If bleaching powder is used, the theoretical chlorine consumption will be the same as for the chlorine gas process.

(2) Handling and metering of the hypochlorites is relatively simple and nonhazardous.

(3) The reaction is more rapid than that with chlorine.

(4) If sodium hypochlorite is used, sludge production is minimized.

This process also is used commercially.

Conversion of Cyanides to Cyanates

The cyanate radical (CNO) reportedly is only about one-thousandth as toxic as cyanide, and many regulatory agencies will accept rather high cyanate concentrations in effluents. The conversion of cyanide to cyanate by chlorine gas is a rapid reaction, requiring only minutes. The reaction which is an intermediate stage in the process for the complete destruction of cyanide by chlroine is:

NaCN	+	Cl_2	+	2NaOH	→	NaCNO	+	2NaCl	+	H_2O .
Sodium cyanide		Chlorine		Sodium hydroxide		Sodium cyanate		Sodium chloride		Water

The process can be carried out in the same type of equipment as that involving the complete destruction of cyanide by chlorine. It also may be conducted batchwise or continuously. Since sludge formation occurs in this process, too, provisions for removing the solids from the treated liquor may be required.

Hypochlorites also can be used for converting cyanides to cyanates by a similar reaction:

NaCN	+	NaOCl	→	NaCNO	+	NaCl .
Sodium cyanide		Sodium hypochlorite		Sodium cyanate		Sodium chloride

Other hypochlorites, such as calcium hypochlorite or bleaching powder can be used in place of sodium hypochlorite. The process is straightfoward and rapid.

For the smaller plater aiming at the partial destruction of cyanide, i.e., the conversion of cyanide to cyanate, the hypochlorite method probably is more suitable than the chlorine method.

Among the other oxidants which have been proposed for the conversion of cyanides to cyanates is hydrogen peroxide.

Hydrogen peroxide reacts with cyanides to form cyanates according to the reaction:

NaCN	+	H_2O_2	→	NaCNO	+	H_2O .
Sodium cyanide		Hydrogen peroxide		Sodium cyanate		Water

Hydrogen peroxide has been used in Europe for treating cyanide wastes from metal-finishing plants. It has an advantage over chlorine or hypochlorite in that additional pollutants (chlorides) are not introduced. However, its use is more expensive than the alkaline chlorination and usually somewhat more expensive than hypochlorite treatment.

Other Methods for Treating Cyanide Wastes

The formation of less toxic cyanide complexes such as ferro and ferricyanides also has been used as a method for disposing of cyanide wastewaters. This process involves the use of iron salts to form complex compounds with the free cyanide in the wastes. Eventually these cyanide complexes are precipitated and removed as a sludge. The use of ferrous sulfate, for example, produces the characteristic dark blue sludge or Prussian blue.

The major advantage of this treatment method is that it is relatively inexpensive where waste ferrous sulfate is available. However, considerable quantities of sludge may be formed and the treated solutions are strongly colored. There also is evidence that ferrocyanides may be decomposed to free cyanide by sunlight. The regeneration of the cyanide under these conditions would contaminate the receiving stream.

This method has received very little acceptance by the industry in this country, but appears to be used in Europe. The complexing process apparently does not completely destroy cyanide under practical operating conditions. Cyanide levels in treated solutions may be as great as 5 to 10 ppm.

Other methods which are described in the literature for the treatment of cyanide wastes include: the formation of cyanide complexes by the use of polysulfides to form relatively nontoxic sulfocyanates, the

conversion of cyanide to cyanate by ozone, the complexation of cyanide by nickel salts to form the highly stable nickel cyanide complex, the biological destruction of cyanide on trickling filters, the destruction of cyanide by irradiation, and the use of techniques such as dialysis and reverse osmosis.

These processes are in various stages of development. Some, such as the use of polysulfides to complex cyanides, or the use of permanganate to destroy cyanides, have been reduced to commercial practice. Some have been merely suggested, i.e., the complexation of cyanide by nickel.

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10 Author(s)

A. K. Reed
J. F. Shea
T. L. Tewksbury
R. H. Cherry, Jr.
G. R. Smithson, Jr.

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27 Abstract

This report describes work which was conducted on the removal of cyanide from plating rinse waters employing various treatment processes. The study consisted of an initial phase in which information was sought by questionnaire and by wastewater analyses on the type of waste produced by smaller electroplating plants. Laboratory studies were conducted on several nonconventional methods for treatment of these wastewaters, including ion flotation, and solvent extraction. A demonstration pilot-plant study also was conducted on the activated carbon process employing actual rinse waters from a zinc cyanide plating operation.

The results of the various phases of the study indicated that activated carbon adsorption for cyanide removal may have practical application in many small plating plants. When combined with pretreatment stages for solids removal, effective elimination of heavy metals also can be expected. Further development of the process was recommended in actual plating plant installations.

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